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<b>1. REPORT DATE (DD-MM-YYYY)</b> 02-11-2010		<b>2. REPORT TYPE</b> Presentation		<b>3. DATES COVERED (From - To)</b>	
<b>4. TITLE AND SUBTITLE</b> Standoff Detection of Persistent Chemical Agents on Surfaces				<b>5a. CONTRACT NUMBER</b> FA8721-05-C-0002	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Emily Meyer				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> MIT Lincoln Laboratory Lexington, MA 02420				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Defense Threat Reduction Agency 8725 John J Kingman Road Fort Belvoir, VA 22060-6201				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b> Distribution Unlimited/Public Release Unlimited					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> Define technology roadmap for standoff surface contamination sensing based on science and technology gaps relative to operational needs and threats. Power Point presentation.					
<b>15. SUBJECT TERMS</b> Chemical Agent Detection, Stand off detection, Sensors, active, passive, LIDAR					
<b>16. SECURITY CLASSIFICATION OF:</b> Unclassified			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>  50	<b>19a. NAME OF RESPONSIBLE PERSON</b> Bryan Horner
<b>a. REPORT</b>	<b>b. ABSTRACT</b>	<b>c. THIS PAGE</b>			<b>19b. TELEPHONE NUMBER (include area code)</b> 7037673379



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MIT Lincoln Laboratory  
244 Wood Street, Lexington, MA 02420-9108

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# Standoff Detection of Persistent Chemical Agents on Surfaces

Emily Meyer, PhD  
Benjamin Ervin, PhD

Group 47  
MIT Lincoln Laboratory

Chemical and Biological Defense  
Science and Technology Conference

November 18, 2010

This work is sponsored by the Defense Threat Reduction Agency and the Joint Science and Technology Office under Air Force Contract #FA8721-05-C-0002. Opinions, interpretations, recommendations and conclusions are those of the authors and are not necessarily endorsed by the United States Government.

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Standoff Chemical-1  
EEM 4/23/2010

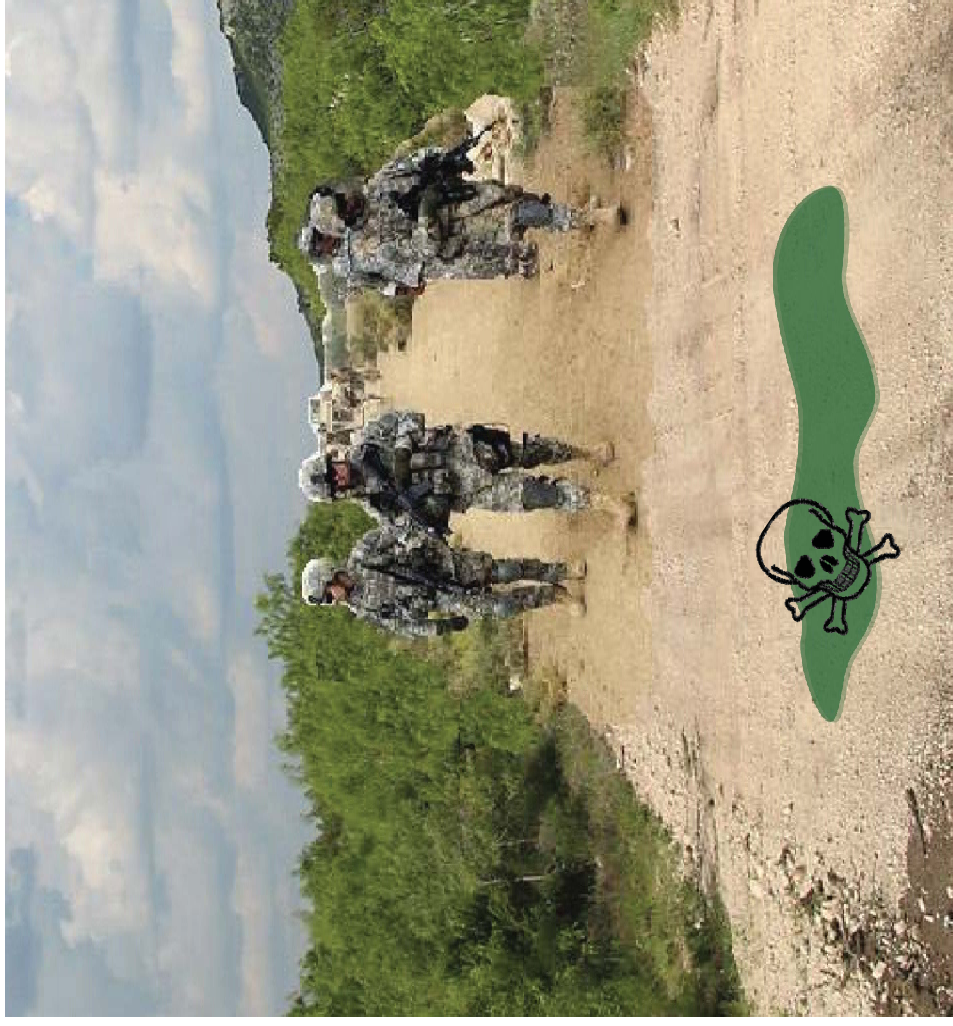
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# Persistent Chemical Agents on Surfaces

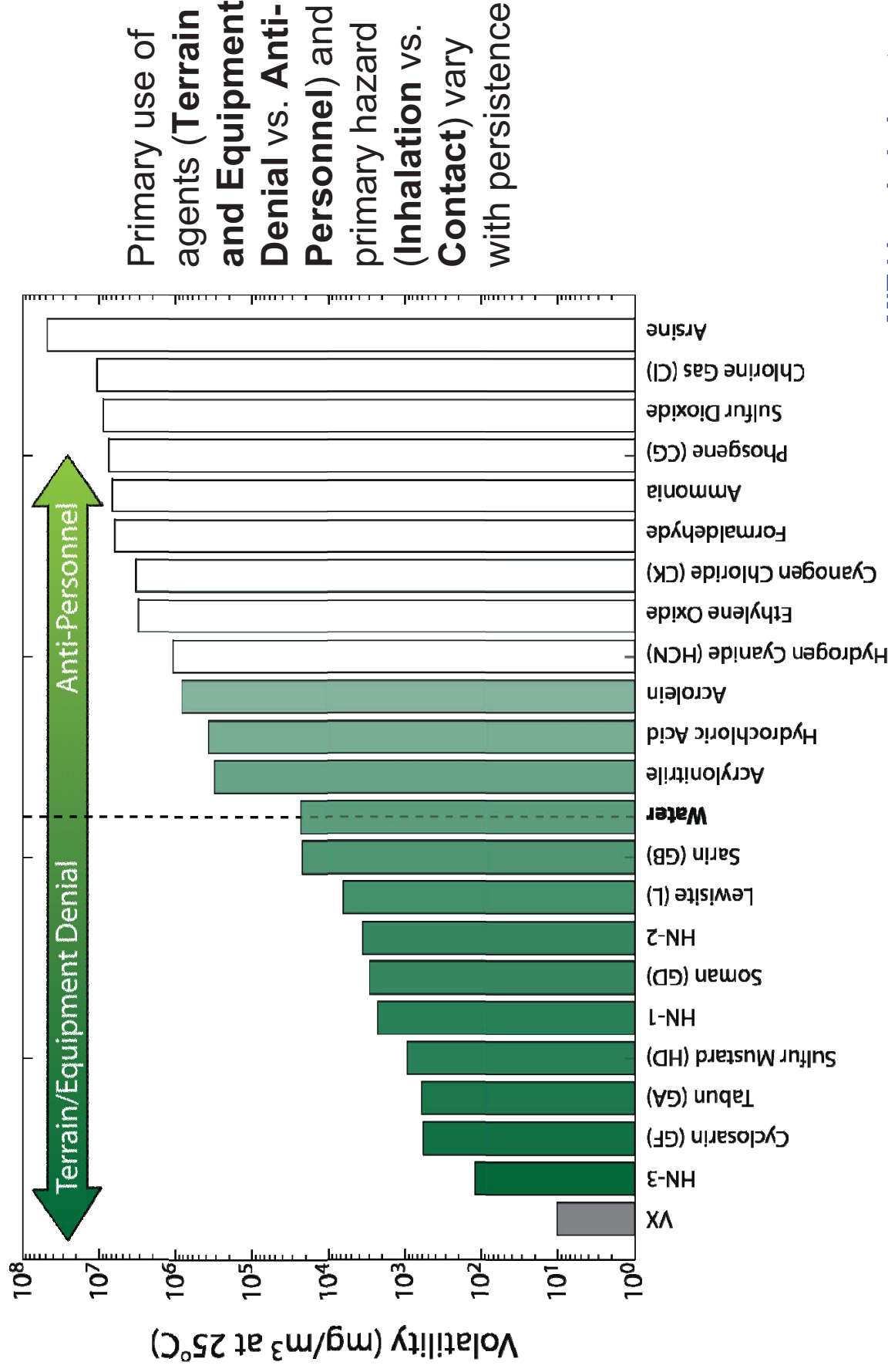
- **Why are persistent agents a serious threat?**
  - Reduces fighting capacity and efficiency (e.g. MOPP gear)
  - Slows military operational tempo (OPTEMPO)
  - Reduces freedom of maneuver
  - Inflicts casualties
  - Persistent



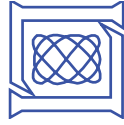
Strong need for ability to **detect** surface contamination, ideally **while avoiding** contamination of equipment or personnel



# Persistent and Nonpersistent Agents



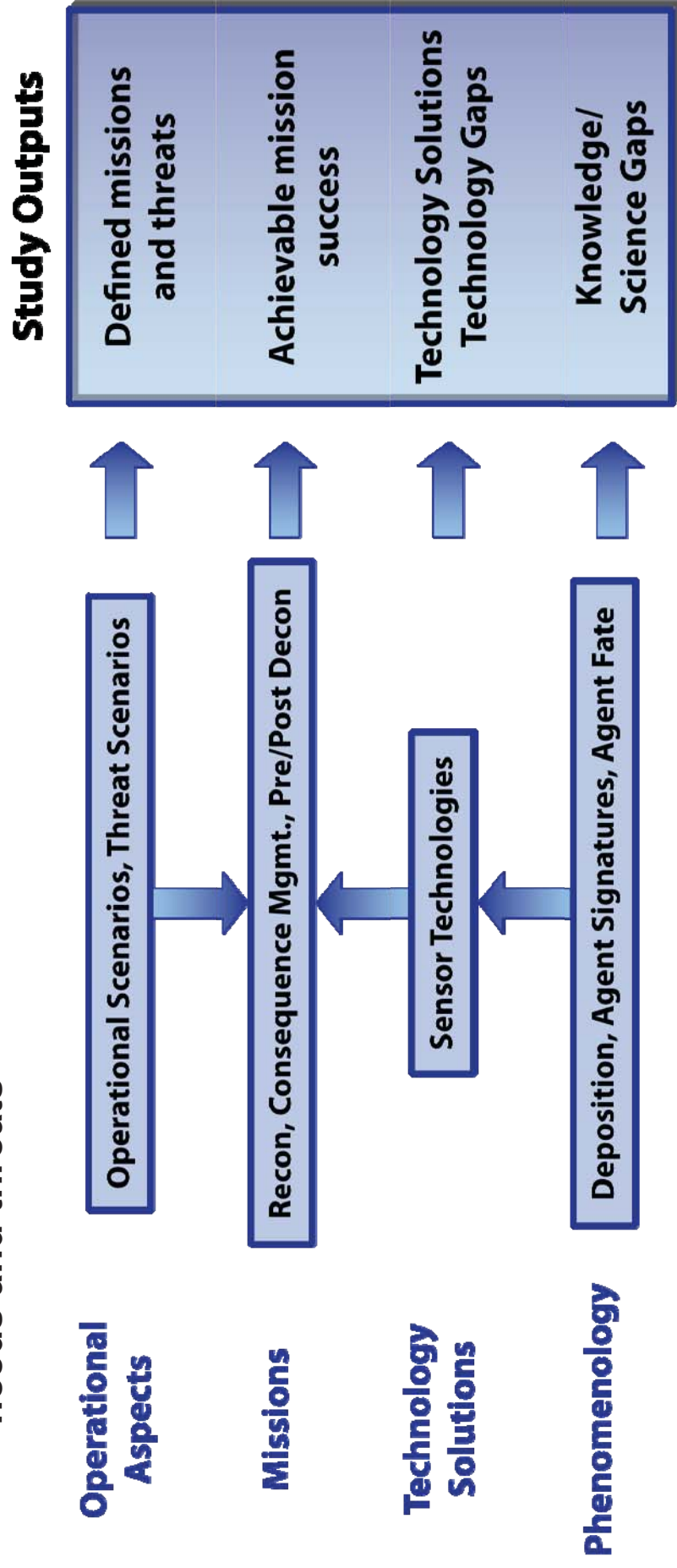




# Study Objectives and Structure:

MIT LL, JHU/APL and ECBC Team

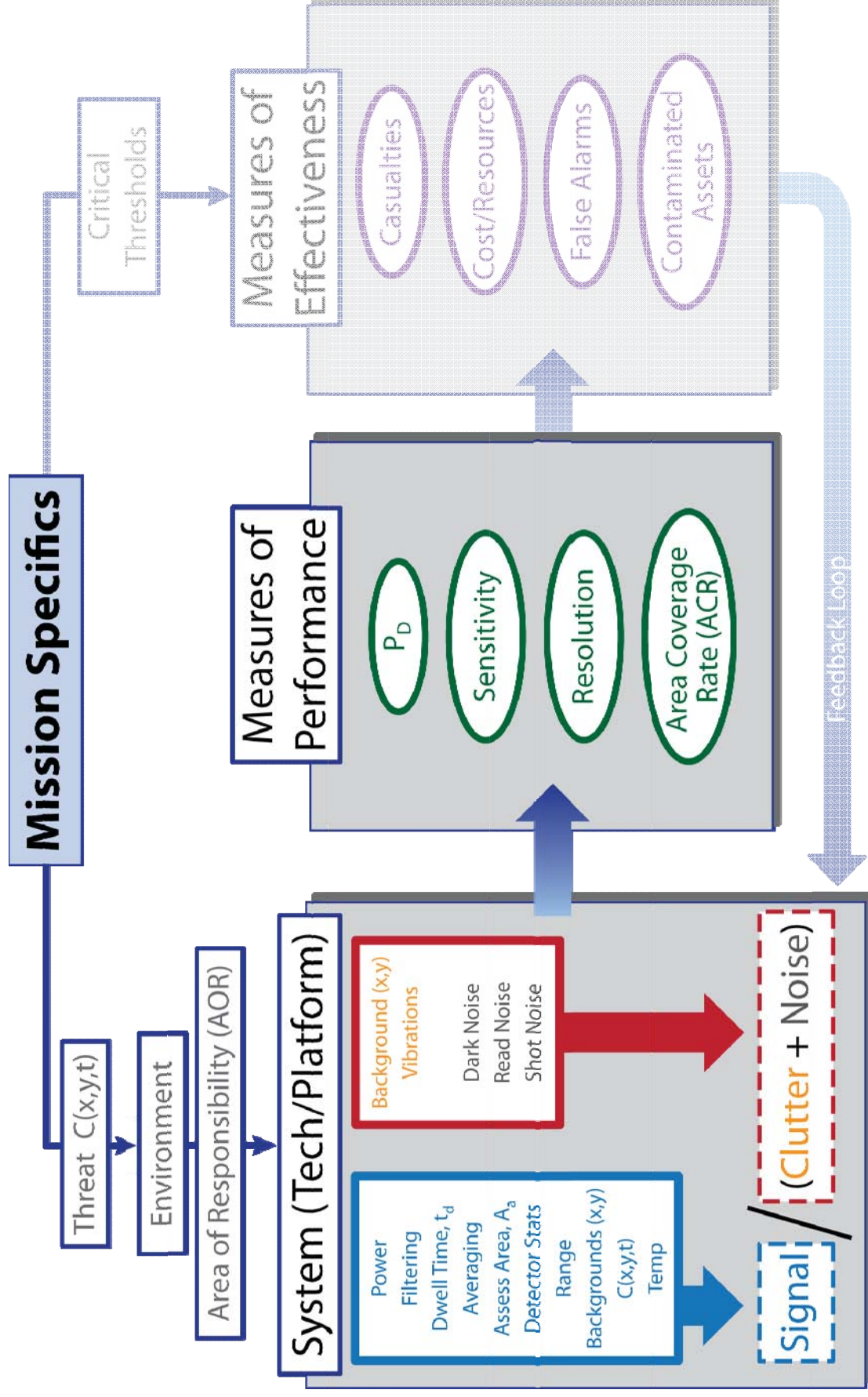
- Define technology roadmap for standoff surface contamination sensing based on science and technology gaps relative to operational needs and threats



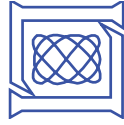
Subset of Results on Sensor Technologies Shown Today



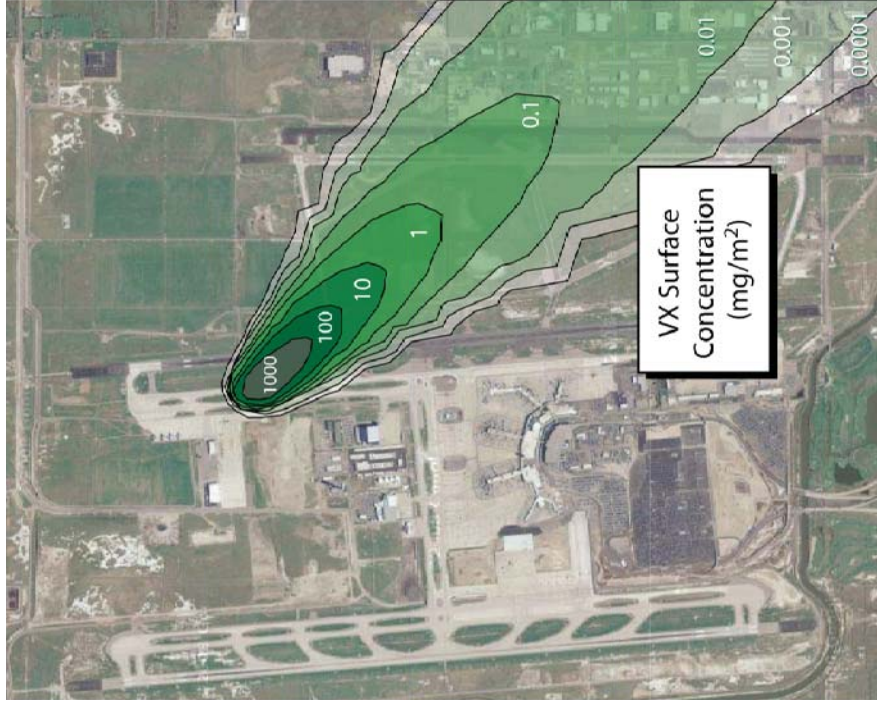
# System Analysis Process







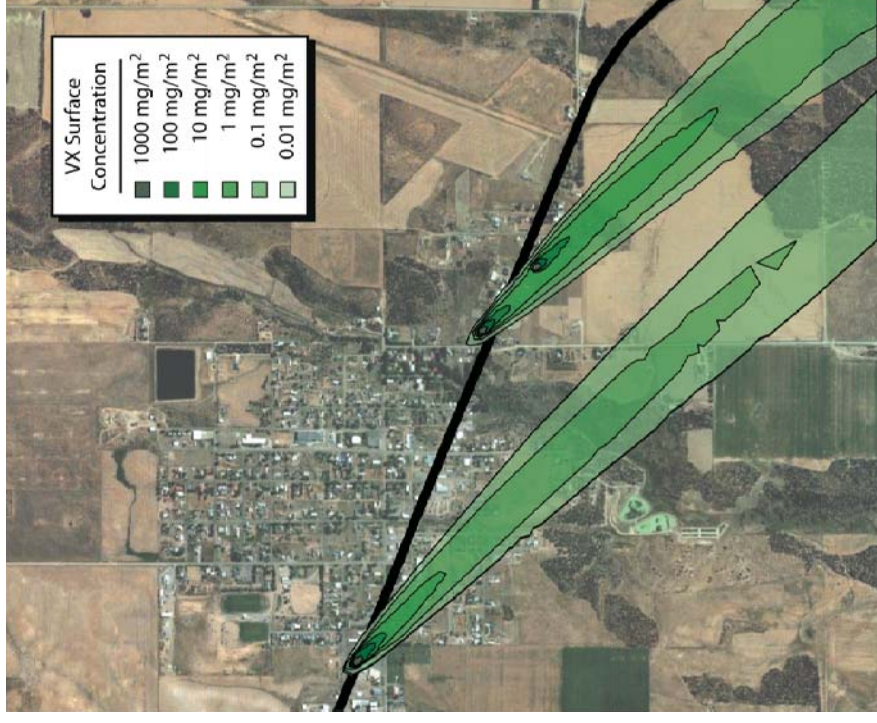
# Mission Scenarios



## Fixed Site

Thickened VX Scud Detonates

**Goal:** Mapping for  
Consequence Management



## Maneuver

VX Sprayers Used Along Route

**Goal:** Warning for  
Contamination Avoidance



# Operational Use Requirements

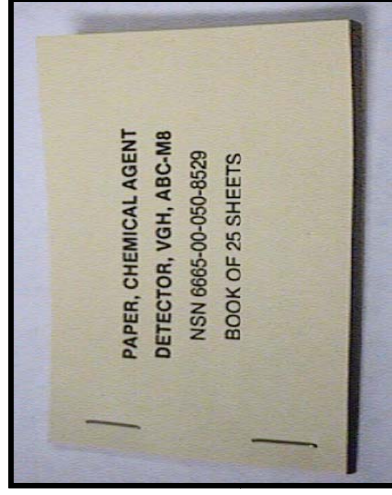
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- Sensitivity: **0.1 mg/m<sup>2</sup>**
  - LD<sub>50</sub> for VX is 3 – 12mg (for adult male)
  - Assume level for safety is 3 orders of magnitude lower
  - Assume area for contact hazard is the surface area of a hand (0.015m<sup>2</sup>)
- Range:
  - Minimum: **10's of meters** to avoid contamination during detection
  - Desired: **100's of meters** to expand architecture possibilities
  - Preferred: **1000's of meters** to accommodate all mission needs
- Speed:
  - **Fixed Site:** Map contamination on a 3.5km x 5km APOD in 25 minutes
    - For 250m x 250m grid, will use **3.5 second** interrogation time
  - **Maneuver:** Warn at a speed of 20kph with time to brake before entering contaminated area
    - Will assume **0.001 second** interrogation time



# Surface Contamination Sensing: Current Systems and Shortcomings

## M8 Colorimetric Paper



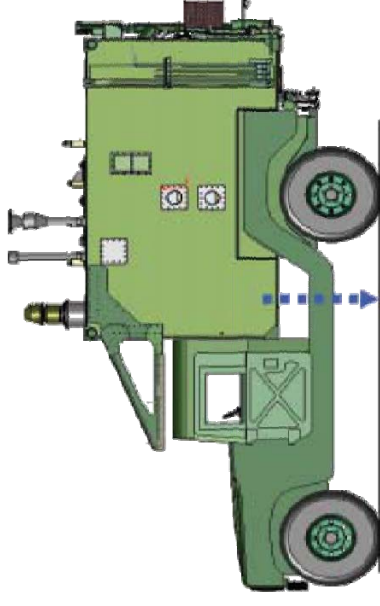
- Standardized in **1963**
- Personnel contamination
- Very slow
- False positives
- Pro: Easy to use

## M93 Fox, double wheeled sampler, Mass Spec



- Approved for fielding in **1995**
- Vehicle contamination
- Slow, 2kph
- Narrow spatial coverage

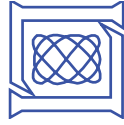
## JCSD (Emerging): Raman System



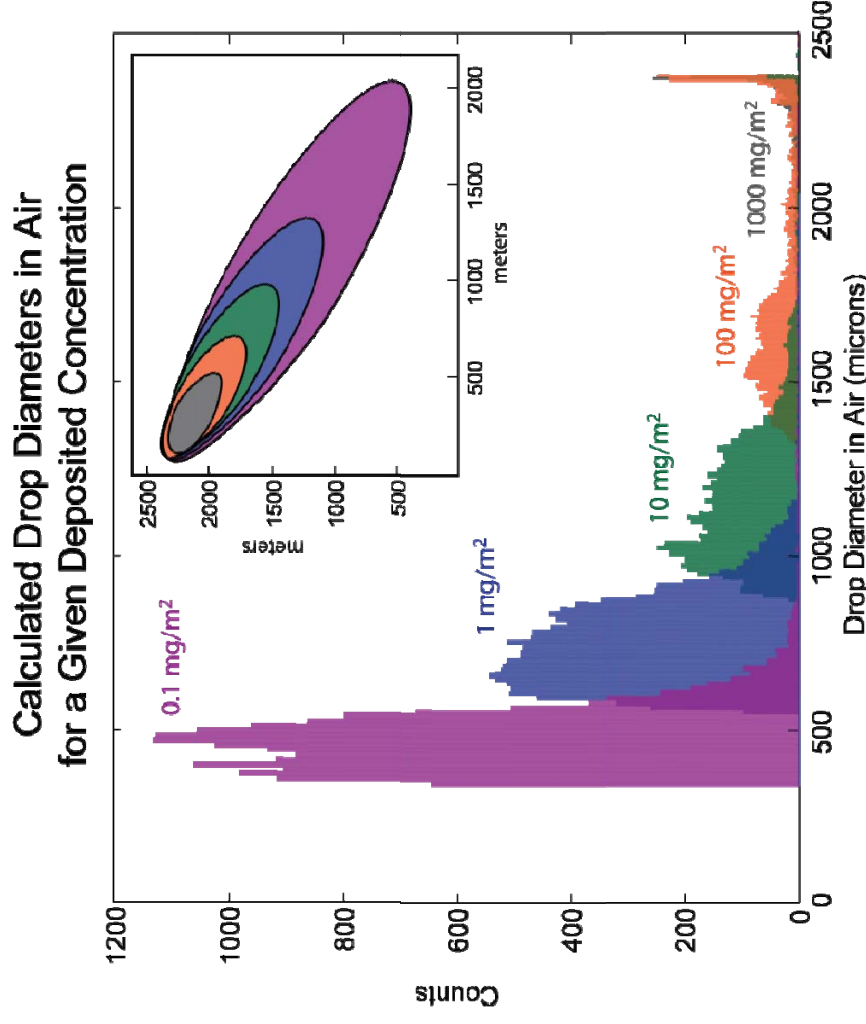
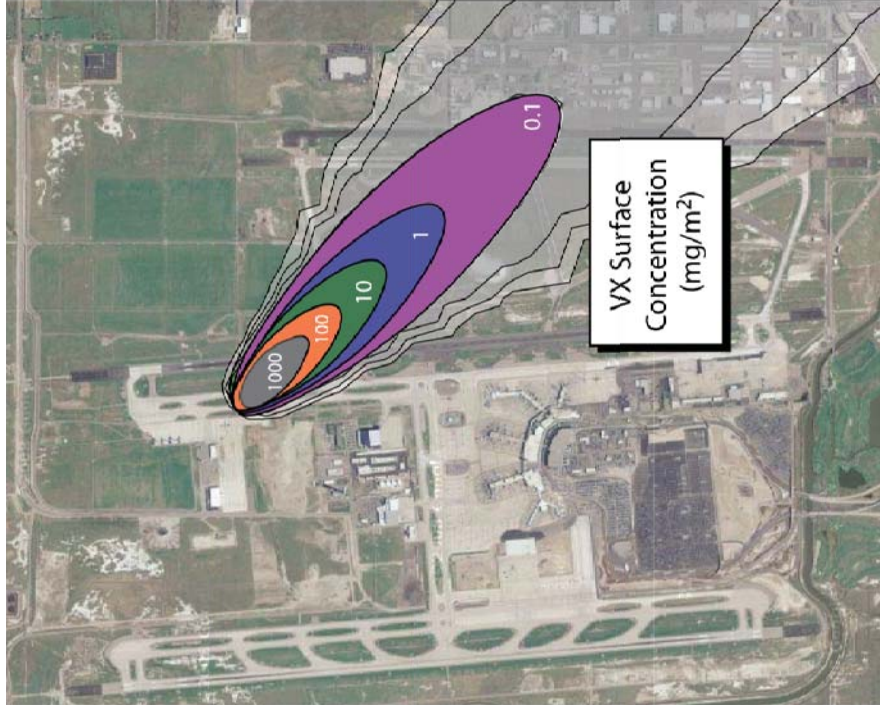
- Developed starting in **2001**
- Vehicle contamination
- Narrow spatial coverage
- Pro: Fast road coverage

Require standoff sensing methods that rapidly map wide areas  
while avoiding personnel/vehicle contamination





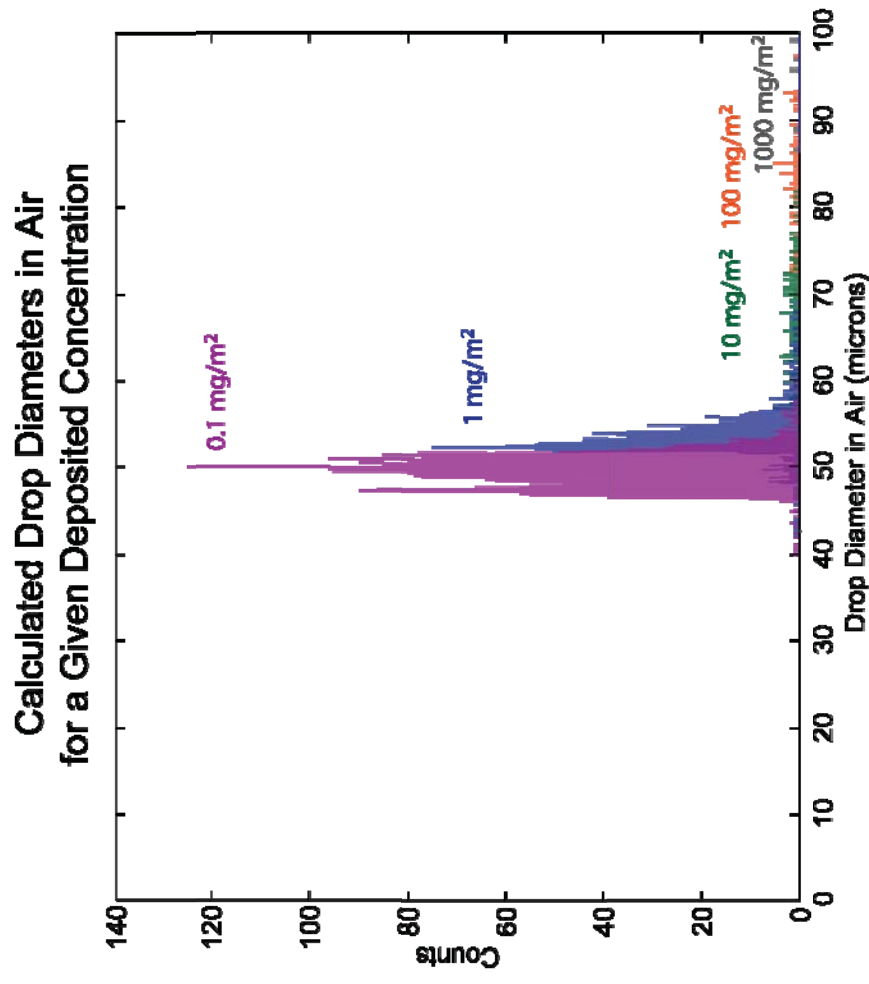
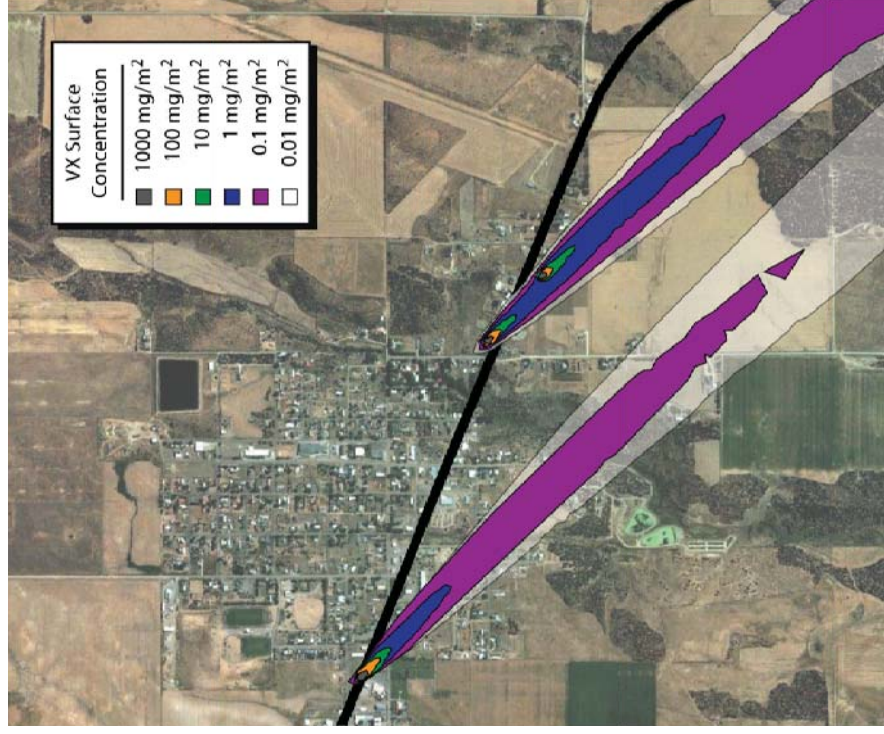
# Fixed Site: Drop Sizes



- Areas of interest are those with concentration  $> 0.1 \text{ mg/m}^2$
- Average drop diameter in lowest concentration region is  $500 \text{ } \mu\text{m}$

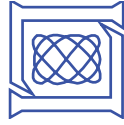


# Maneuver: Drop Sizes

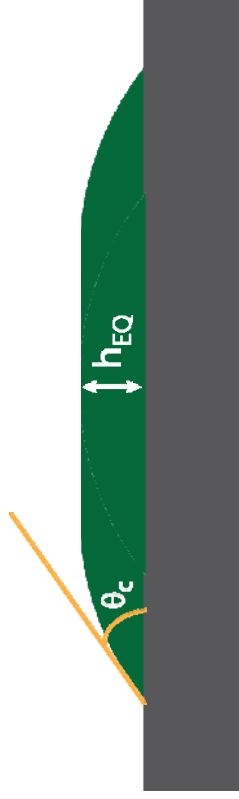


- Sprayers produce much smaller drop sizes than on the Fixed Site
- Average drop diameter in lowest concentration region is 50  $\mu\text{m}$



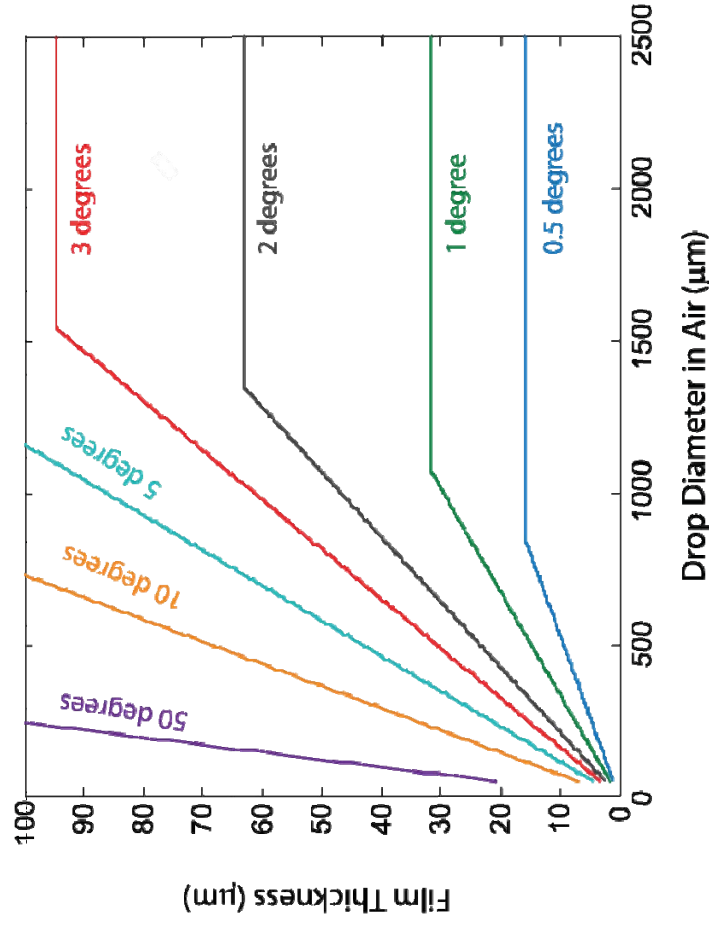


# Drop and Film Characteristics



$$h_{EQ} = \sqrt{\frac{2\gamma(1 - \cos \theta_c)}{\rho g}}$$

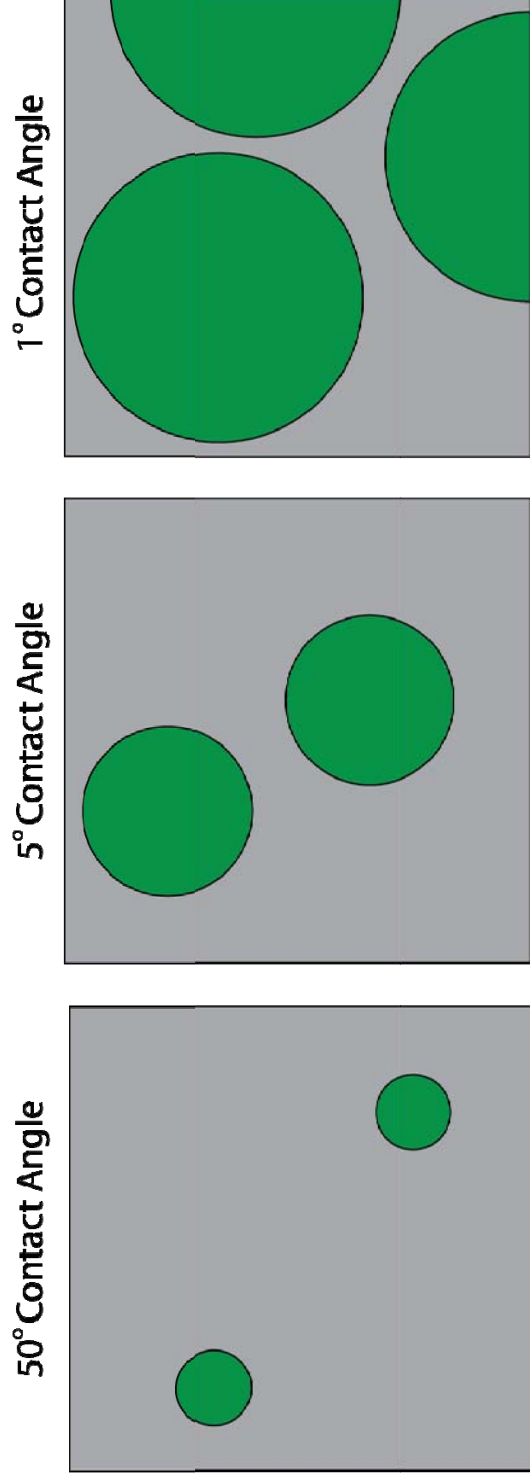
Peak Height of Surface Film  
vs. Drop Size and Contact Angle



- Drops will spread as spherical caps until equilibrium thickness ( $h_{EQ}$ ) is reached, at which point they begin to spread as films of thickness  $h_{EQ}$
- Contaminant distribution on substrate will depend on dissemination method and substrate-contaminant wetting properties



# Drop Spreading



- Low contact angles will result in larger contaminant surface area, larger percentage of substrate covered in contaminant
- Wetting properties will vary between contaminants and between substrates
- Values are not readily available in the open literature, so contact angle is parameterized in this analysis

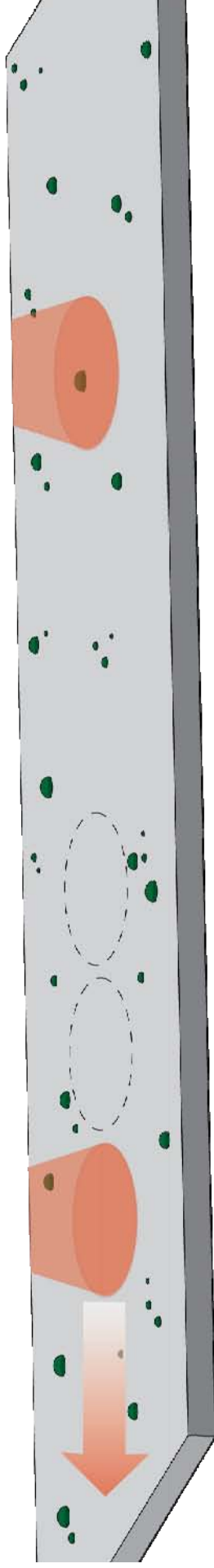


# Probability of Detection ( $p_d$ )

System  $p_d$  is dependent on:

$p_{\text{drop}}$ : Probability drop is interrogated

$p_{\text{sensor}}$ : Probability sensor detects drop if interrogated



$$p_d = p_{\text{drop}} \cdot p_{\text{sensor}}$$

System  $p_d$  could be very poor even with a “perfect” sensor ( $p_{\text{sensor}} = 1$ )



# Probability of Detection ( $p_d$ )

$$p_d = p_{\text{drop}} \cdot p_{\text{sensor}}$$

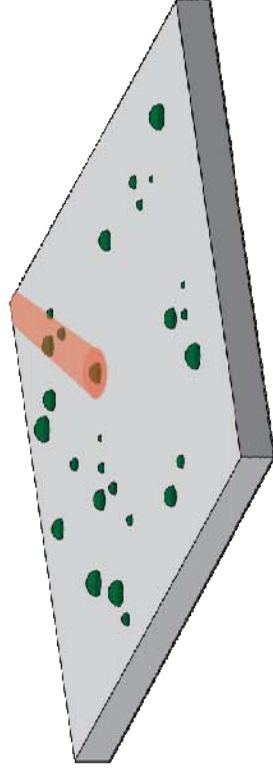
High Sensitivity

Low Area Coverage Rate

Low Probability of Encountering a Drop

$p_{\text{drop}} \downarrow$

$p_{\text{sensor}} \uparrow$



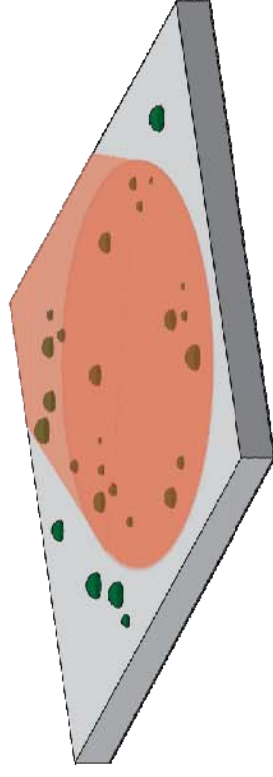
Lower Sensitivity

Higher Area Coverage Rate

Higher Probability of Encountering a Drop

$p_{\text{drop}} \uparrow$

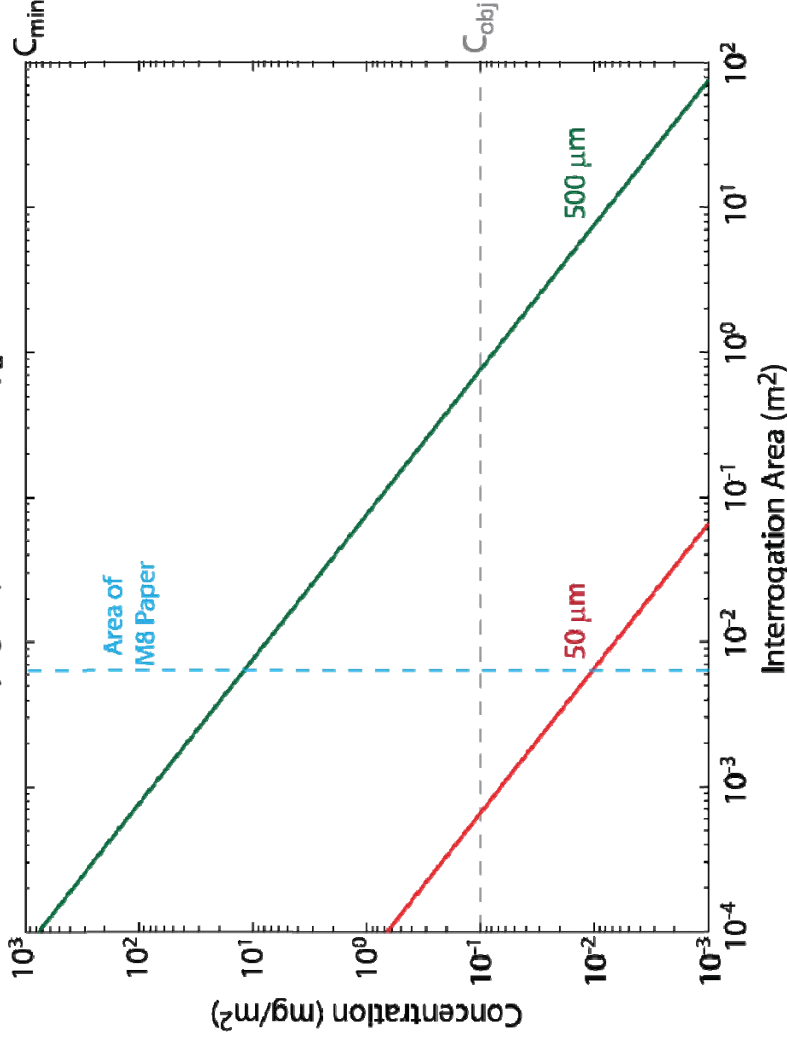
$p_{\text{sensor}} \downarrow$





# Choice of Interrogation Area

Detectable Concentration vs. Standoff Distance  
Varying Drop Diameter in Air,  $P_d = 0.95$



- Interrogation area required for a  $p_d$  of 95% will depend on drop size and contaminant concentration
- For larger drops, a higher concentration is required
- A typical sheet of M8 paper (area = 65 cm<sup>2</sup>) will not be able to detect  $C_{obj}$  for the Fixed Site with sufficiently high  $p_d$

Desired detection capability will define  
necessary size of interrogated area



# Outline

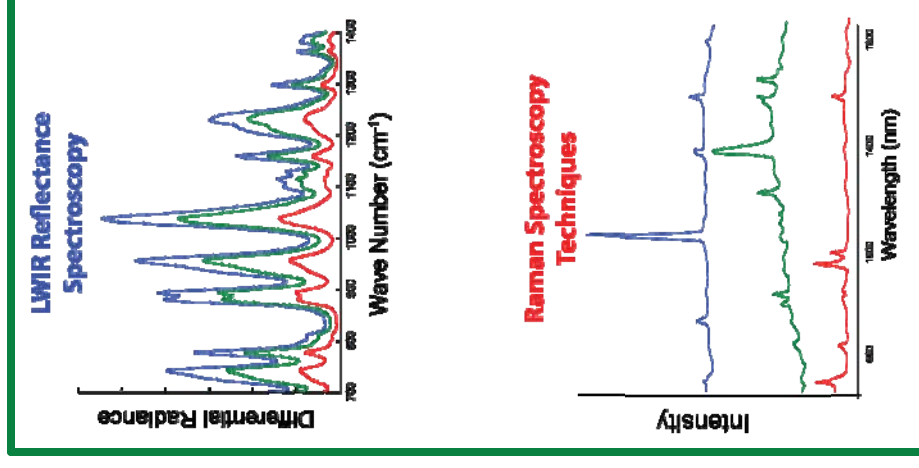
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- **Example Mission Scenarios**
  - Current Technologies
  - Operational Requirements
  - Concentration Profiles
  - Contaminant Phenomenology
- **Potential Standoff Technologies**
- **Application to Scenarios: Fixed Site**
  - Raman Spectroscopy
  - Active and Passive LWIR Spectroscopy
- **Application to Scenarios: Maneuver**
  - Active and Passive LWIR Spectroscopy
- **Conclusions**



# Potential Technologies for Standoff CWA Detection

- Consider technologies that have been demonstrated to be capable of “true” standoff CWA detection
  - No sample collection
  - No special substrates required
  - Nothing but photons interacting with contaminant
- Evaluate technologies based on:
  - Sensitivity (SNR, Range, Dwell Time)
  - Selectivity (Interferents, clutter)
  - SWAP (platform compatibility)
  - Maturity (TRL  $\geq 2$  required)

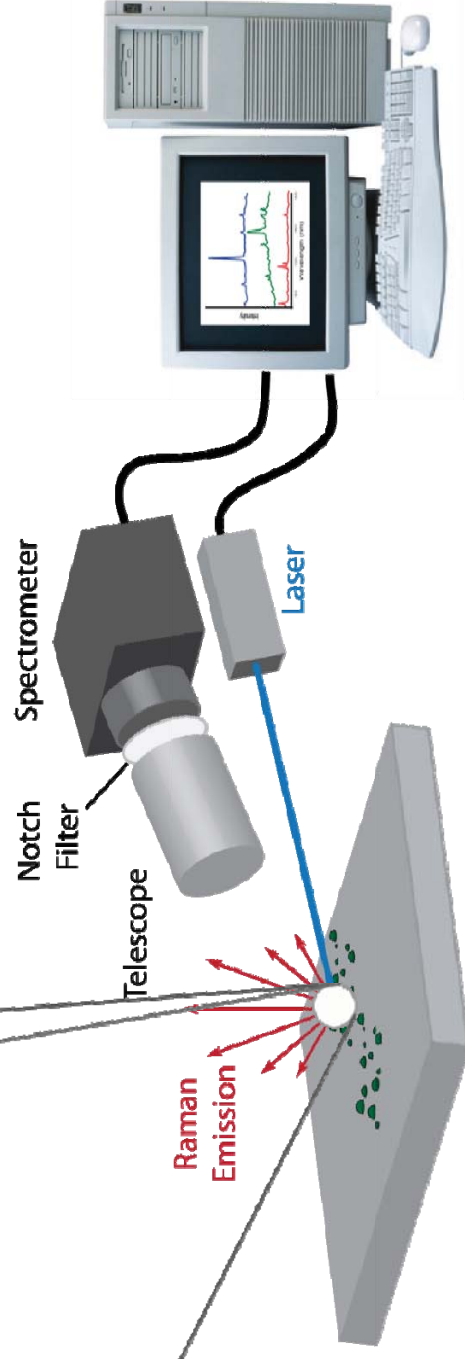
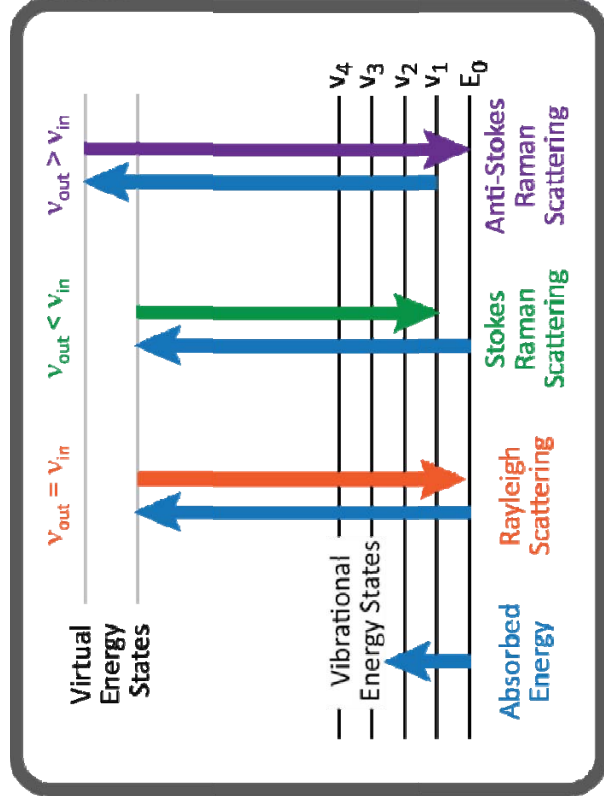






# Potential Detection Technology: Raman

- Laser photon excites molecule into virtual state
- Raman scattering when frequency of photon emitted as molecule relaxes is shifted ( $\nu_{\text{out}} > \nu_{\text{in}}$  for Stokes,  $\nu_{\text{out}} < \nu_{\text{in}}$  for Anti-Stokes)
- **Highly specific** technique
- Signal is typically fairly weak at eye-safe laser power

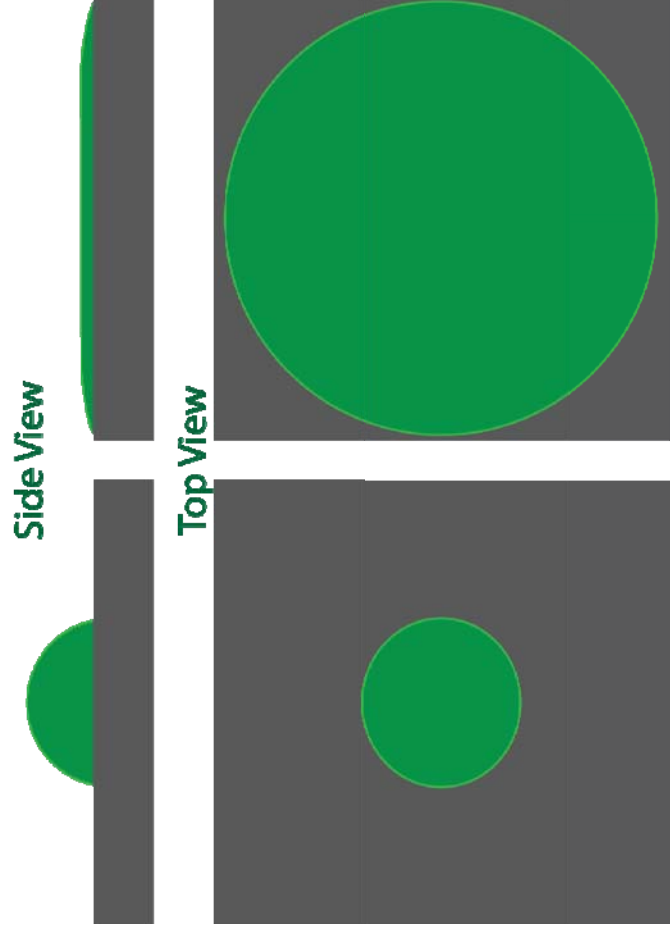




# Optimizing Raman Signal: Importance of Deposition Details (VX)

$$\text{Photons Detected} \rightarrow N_{\text{out}} = \Omega N_{\text{in}} \sigma_R C_{\text{eff}}$$

Solid Angle (points to  $\Omega$ )      Raman Cross-Section (points to  $\sigma_R$ )      Incident Photons (points to  $N_{\text{in}}$ )      Contaminant Concentration (points to  $C_{\text{eff}}$ )

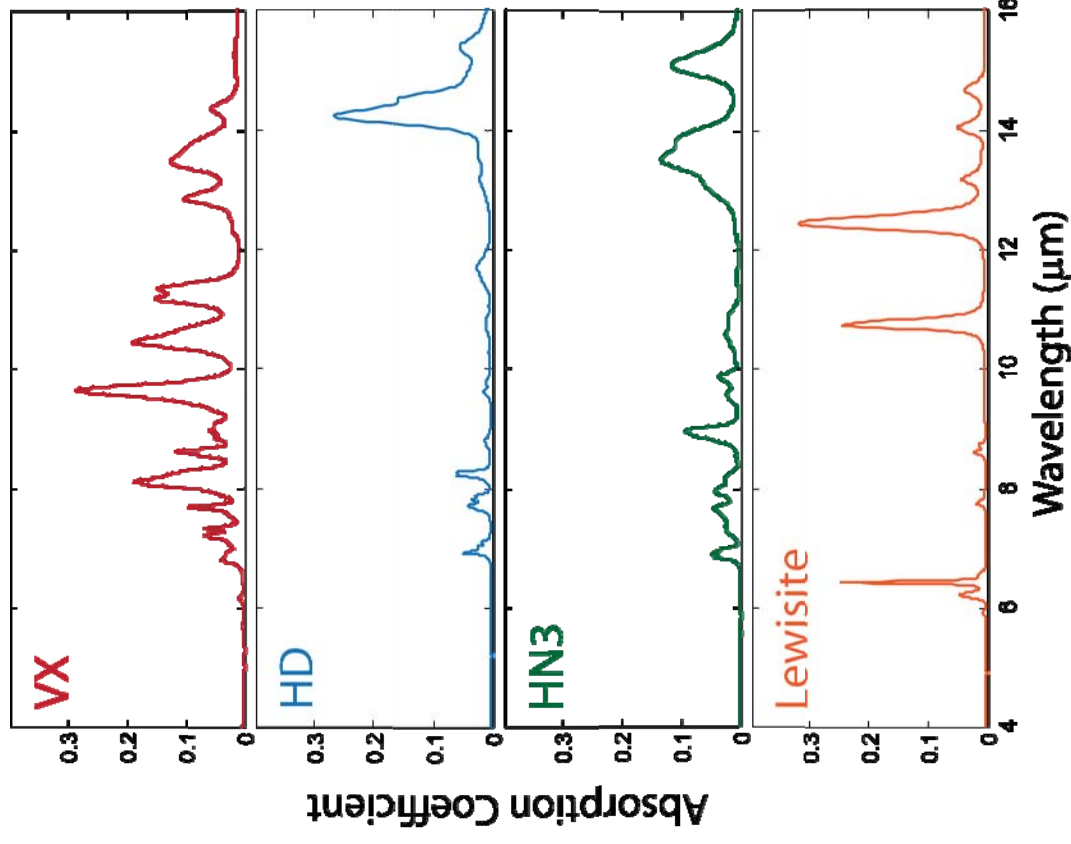
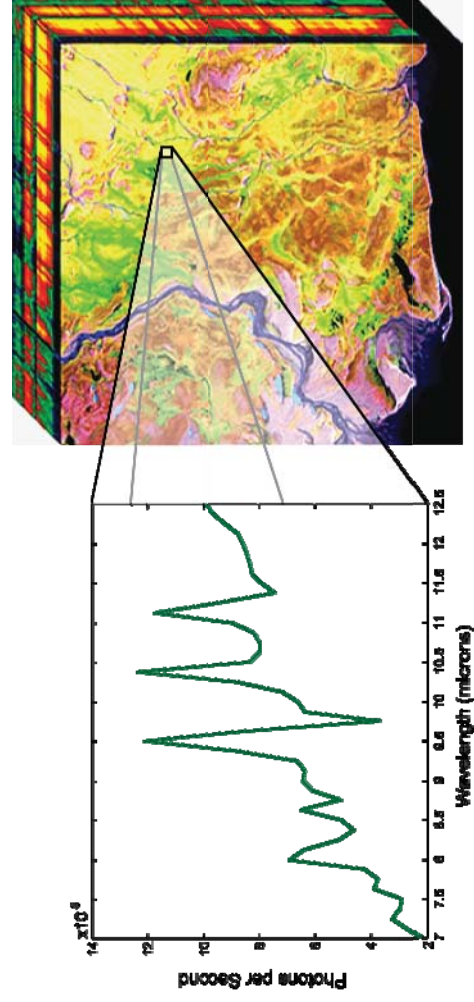


- For wavelengths at which VX absorbs strongly (e.g. deep UV), only the first micron of molecules is expected to contribute to Raman signal
- Same **volume** can have very different **surface area** depending on wetting



# Potential Detection Technology: LWIR Reflectance

- CWAs have strong absorption features in the LWIR, which also coincides with atmospheric window
- Acquire reflectance data vs.  $\lambda$  either at a single point or at each pixel in a hyperspectral image to map out contamination
- Active or Passive techniques can be used

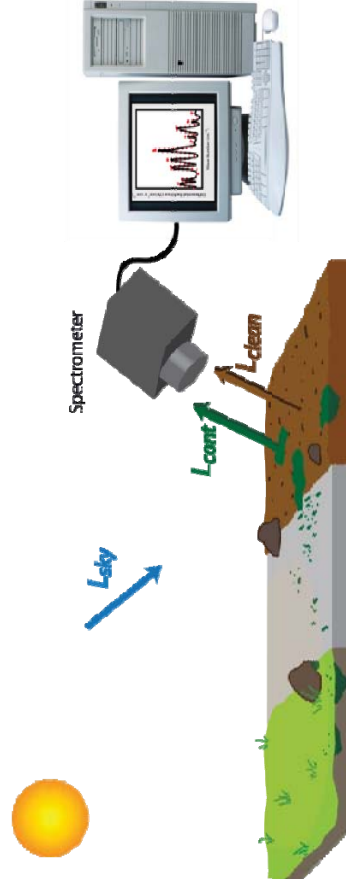




# Potential Detection Technology: Passive and Active LWIR Reflectance

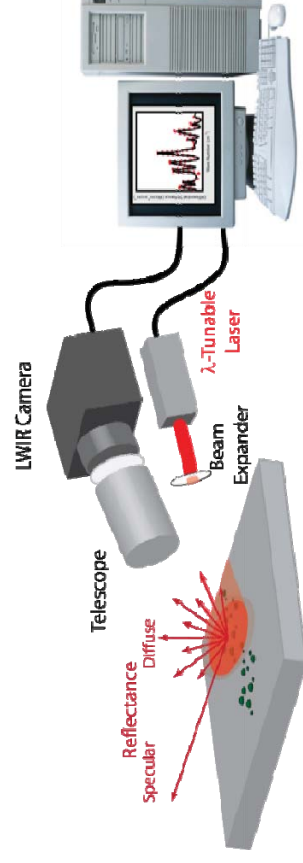
## Passive

- Differential radiance determined by measuring difference in radiance between clean and contaminated areas with an FTIR spectrometer
- Primarily an outdoor technique
- Sensitive to environmental factors
- Imaging detectors provide wide area coverage



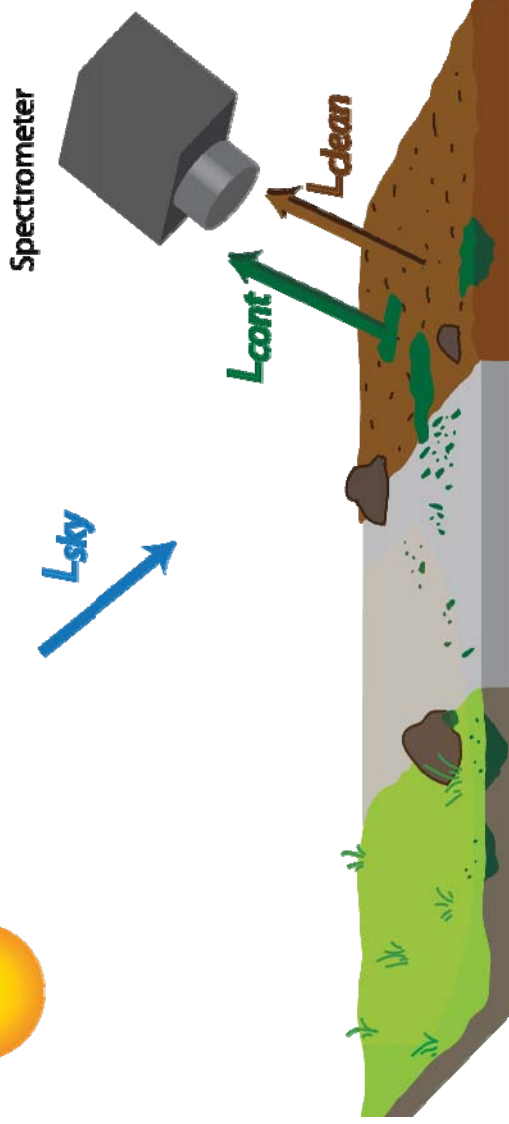
## Active

- Either tunable laser or radiant heater as source
- Record reflectance in a given direction with IR Camera for laser source or imaging FTIR spectrometer for heater
- Strong angular dependence presents problems in field testing
- Active area of research





# Passive LWIR Signal Equations



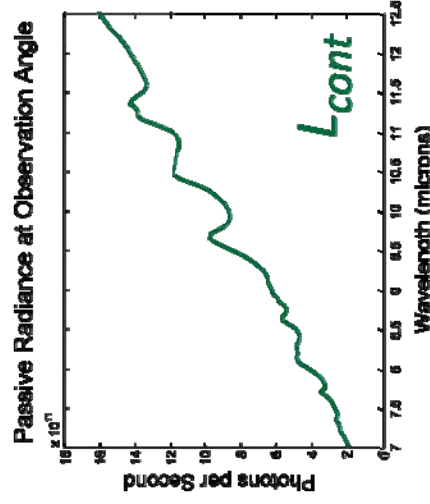
$$L_{clean} = B - R_{surf}(B - L_{sky})$$

$$L_{cont} = B - R_{cont}(B - L_{sky})$$

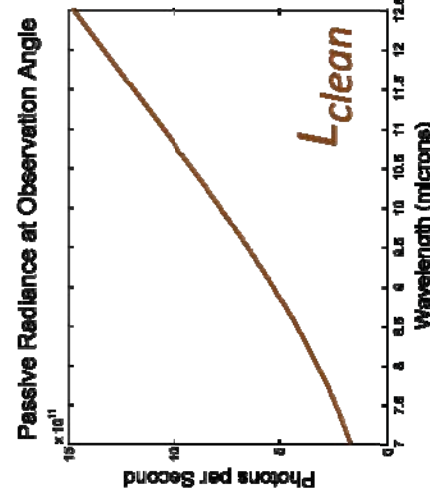
$$B = \frac{2hc^2v^3}{\exp(hcv/kT) - 1} \quad \text{(Planck Radiance of surface)}$$

Differential Radiance:

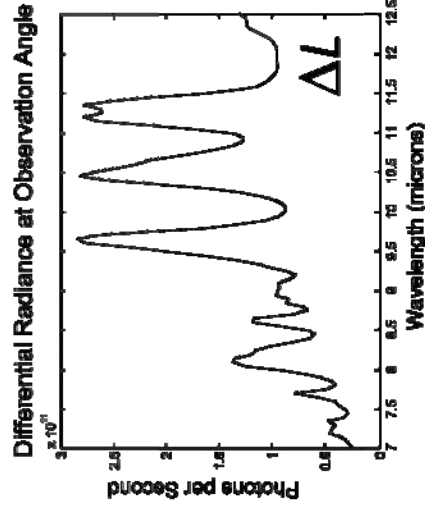
$$\Delta L = (R_{surf} - R_{cont})(B - L_{sky})$$



—



=





# Active LWIR Signal Equations

User-Controlled

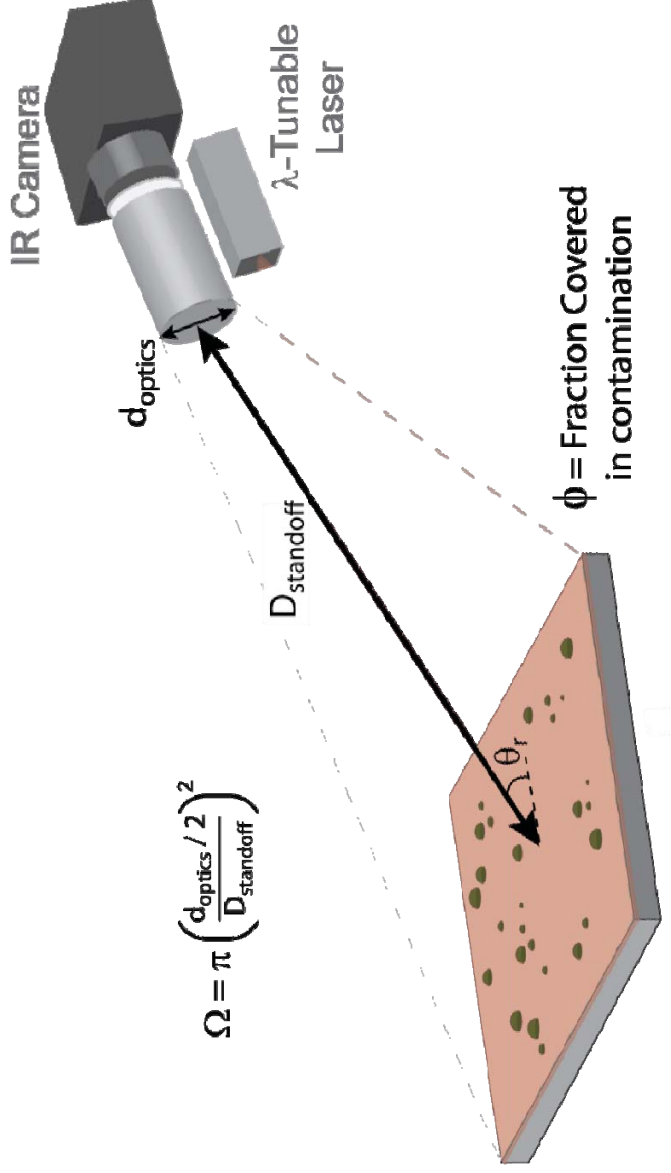
System Properties

$R_{\text{cont}}$

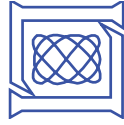
## User-Controlled

### Parameters:

- Laser power ( $P_{\text{laser}}$ ) limited by SWaP, eye-safety
- Interrogation time ( $\tau$ ) limited by mission time constraints
- Solid angle ( $\Omega$ ) limited by required standoff distance, size constraints on optics







# Signal Equations: Reflectivity

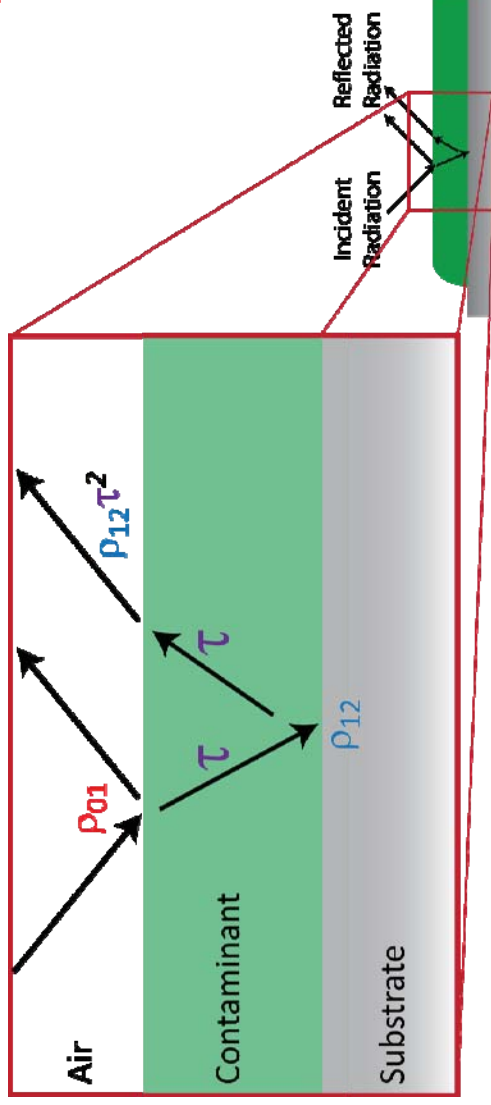
$$R_{cont} = (\rho_{cont})(\rho_{cont}^*)$$

$$\text{where } \rho_{cont} = \frac{\rho_{01} + \rho_{12}\tau^2}{1 + \rho_{01}\rho_{12}\tau^2}$$

$\rho_{01}$  = Air-Contaminant Interface Reflectance Amplitude

$\rho_{12}$  = Contaminant-Substrate Interface Reflectance Amplitude

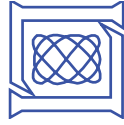
$\tau$  = Contaminant Single-Pass Transmission



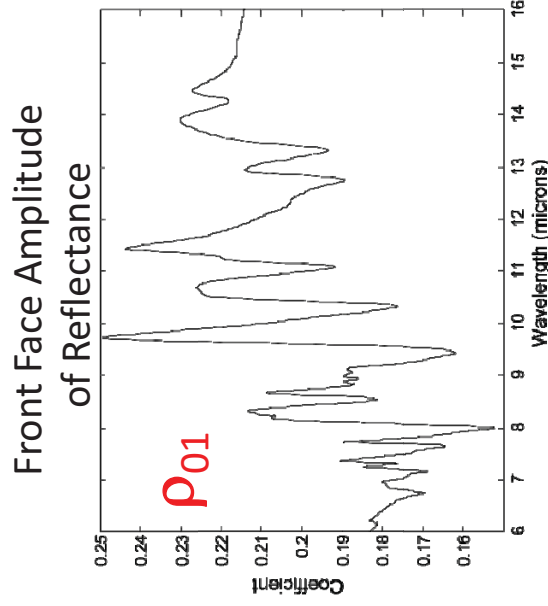
- Substrate reflectivity ( $\rho_{12}$ ) scales double-pass transmission ( $\tau^2$ )
- For a minimally reflective substrate, the air-contaminant reflectance amplitude ( $\rho_{01}$ ) will dominate
- For a highly reflective substrate with sufficient transmission, absorption features from the double-pass transmission will dominate

Reflectance properties are a function of both **substrate** and **contaminant** properties, and determine **signal quality** at detector





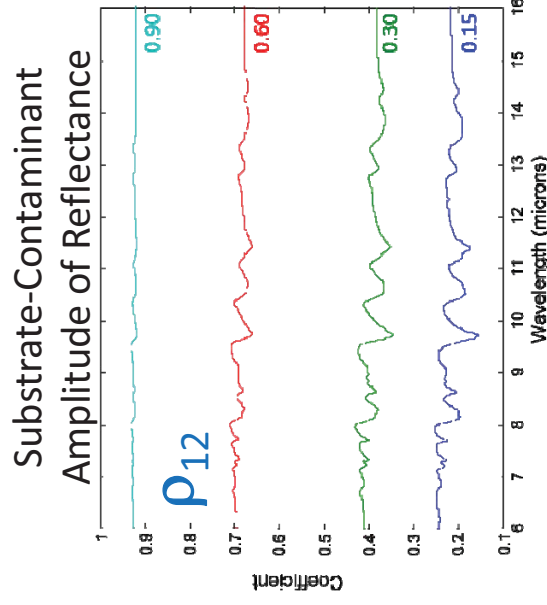
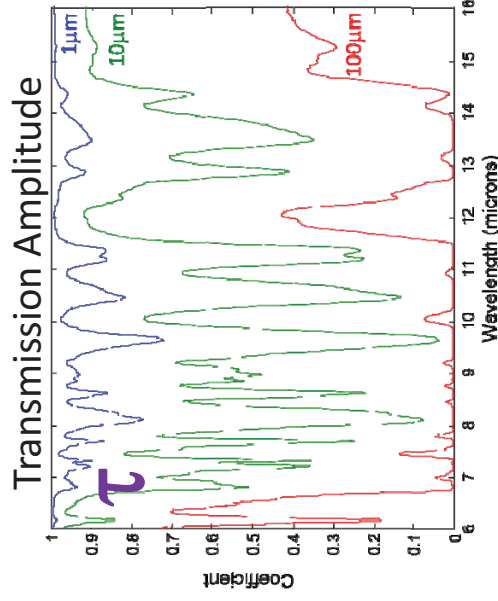
# Transmission and Reflectance Coefficients (VX Example)



$$R_{cont} = (\rho_{cont})(\rho_{cont}^*)$$

$$\text{where } \rho_{cont} = \frac{\rho_{01} + \rho_{12}\tau^2}{1 + \rho_{01}\rho_{12}\tau^2}$$

## Single-pass

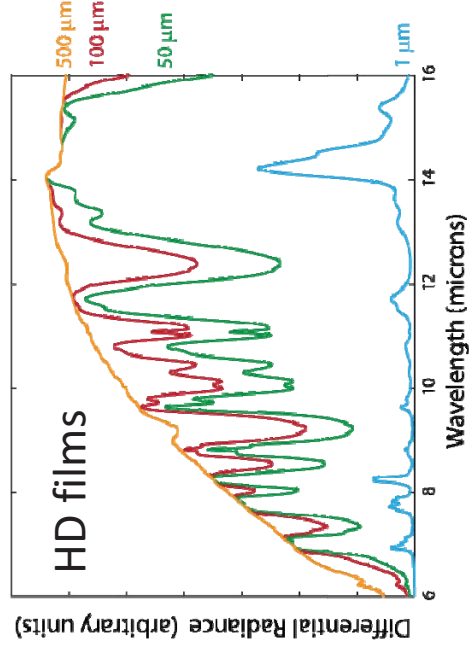
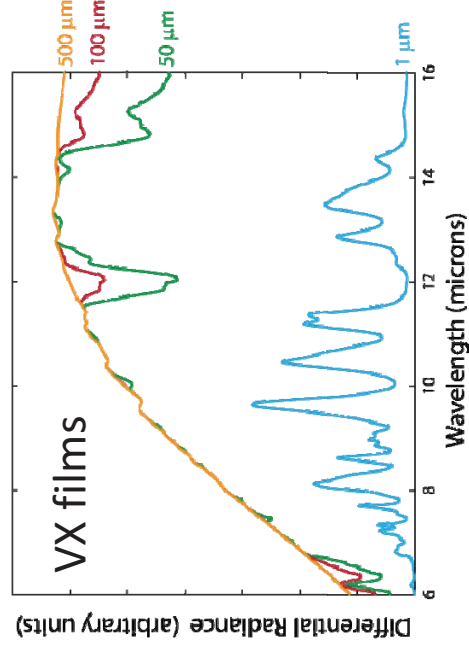


- Absorption spectral features (seen in  $\tau$ ) become less clear as film thickness increases
- Front face reflectance amplitude ( $\rho_{01}$ ) is relatively small compared to other two parameters
- Film thickness and contaminant-substrate reflectance amplitude will combine to determine relative strength of  $\rho_{12}\tau^2$  term

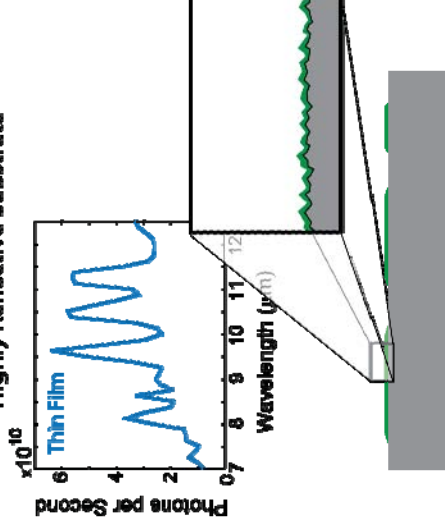


# Detection Capabilities and Contaminant Distribution: Signal Quality

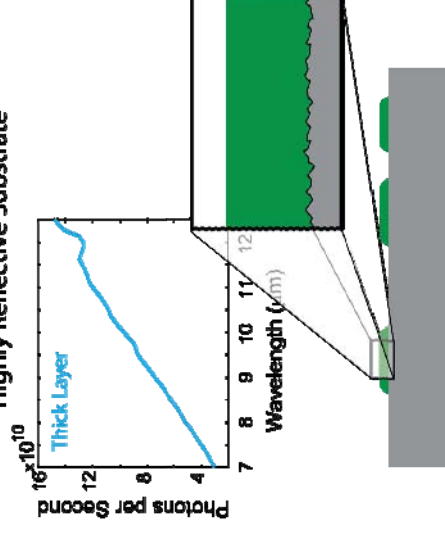
Signal can be **strong**, but without clear spectral features and thus **low-quality**



Thin VX Film on a Highly Reflective Substrate



Thick VX Film on a Highly Reflective Substrate





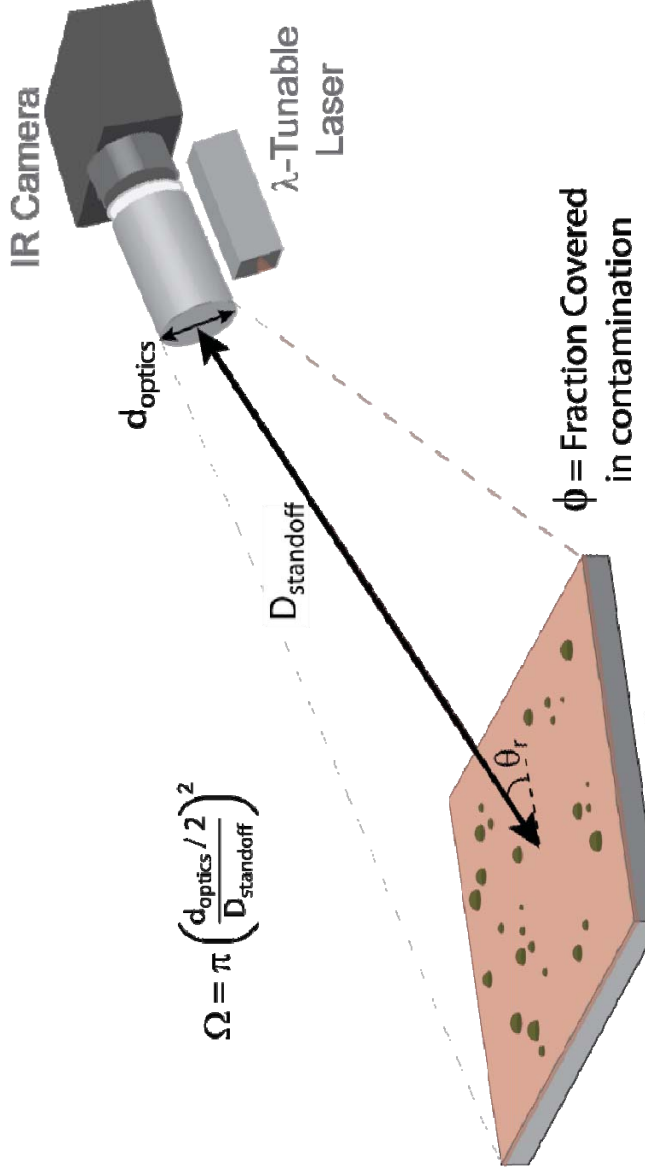
# Active LWIR Signal Equations: Scattering Properties

User-Controlled

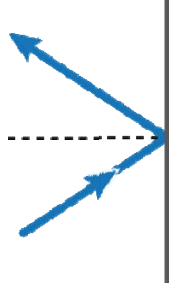
System Properties

$$N_{\text{cont}} = P_{\text{laser}} \cdot \tau \cdot \Omega \cdot f_{\text{BRDF}} \cdot [(1 - \phi) \cdot R_{\text{clean}} + \phi \cdot R_{\text{cont}}]$$

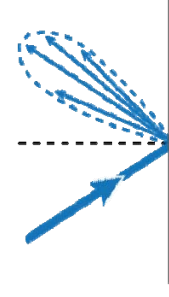
$$N_{\text{clean}} = P_{\text{laser}} \cdot \tau \cdot \Omega \cdot f_{\text{BRDF}} \cdot R_{\text{clean}}$$



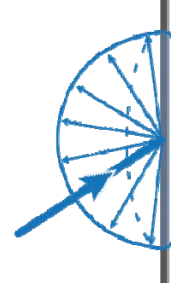
Scattering Profiles ( $f_{\text{BRDF}}$ )



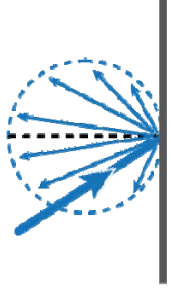
Specular



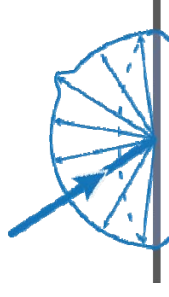
Quasi-Specular



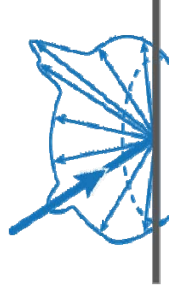
Diffuse



Lambertian



Primarily Diffuse



Less Idealized

Scattering properties are a function of **substrate**, and determine  
signal strength at collocated detector



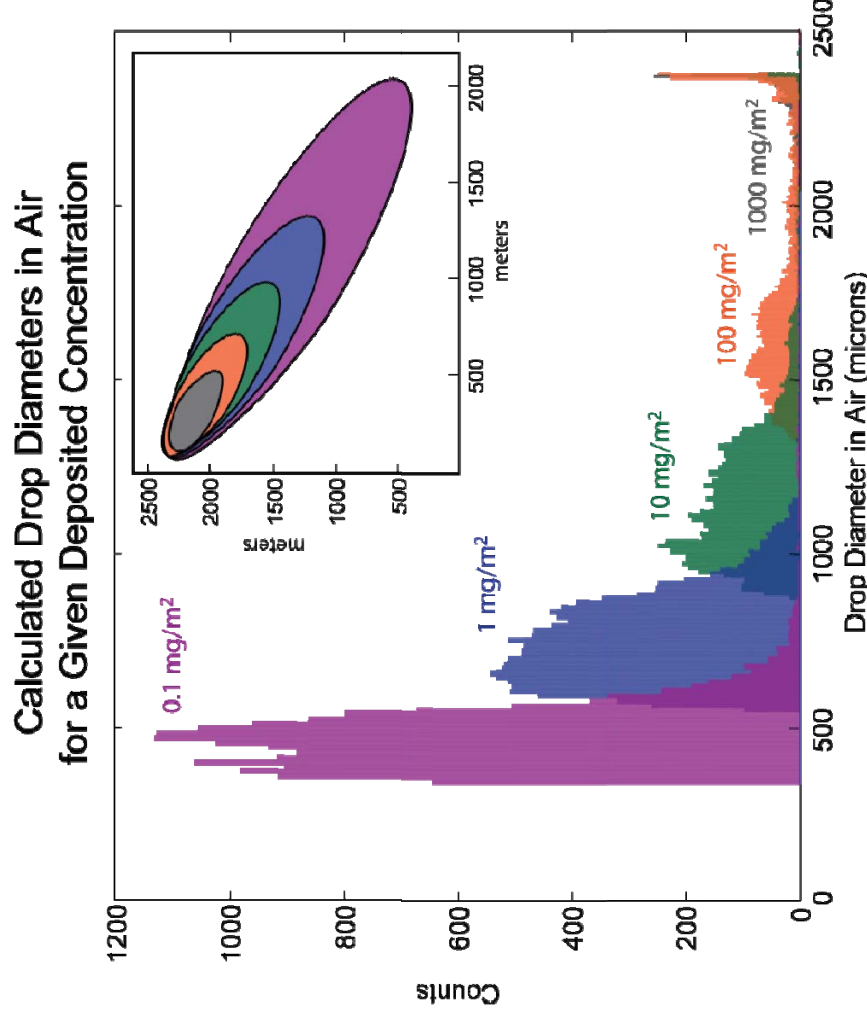
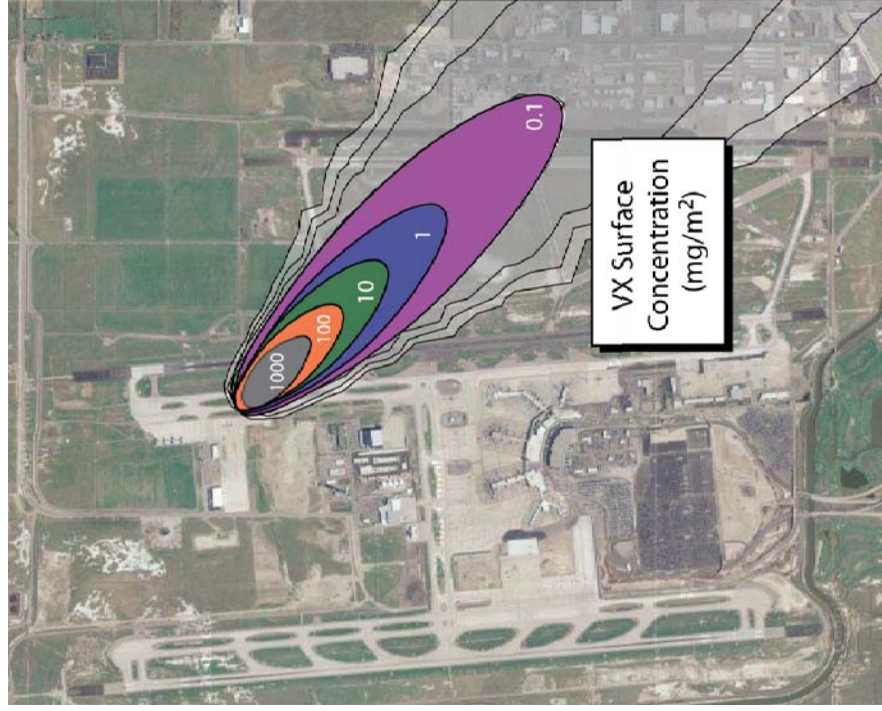
# Outline

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- **Example Mission Scenarios**
  - Current Technologies
  - Operational Requirements
  - Concentration Profiles
  - Contaminant Phenomenology
- **Potential Standoff Technologies**
  - Raman Spectroscopy
  - Active and Passive LWIR Spectroscopy
- **Application to Scenarios: Fixed Site**
  - Raman Spectroscopy
  - Active and Passive LWIR Spectroscopy
- **Application to Scenarios: Maneuver**
  - Active and Passive LWIR Spectroscopy
- **Conclusions**



# Fixed Site

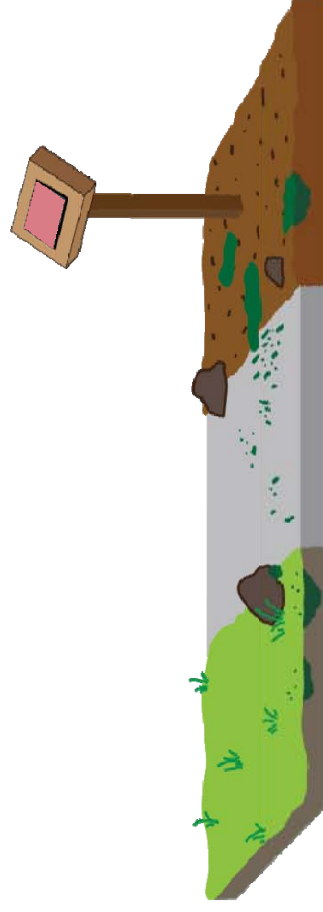
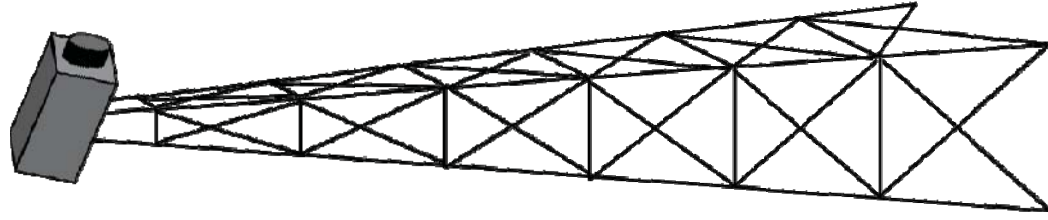


- Baseline Technology: **M8 Paper**
- Can take advantage of fixed site by pre-placing cooperative or carefully chosen substrates around the base



# Fixed Site: Tower Platform w/ Stands

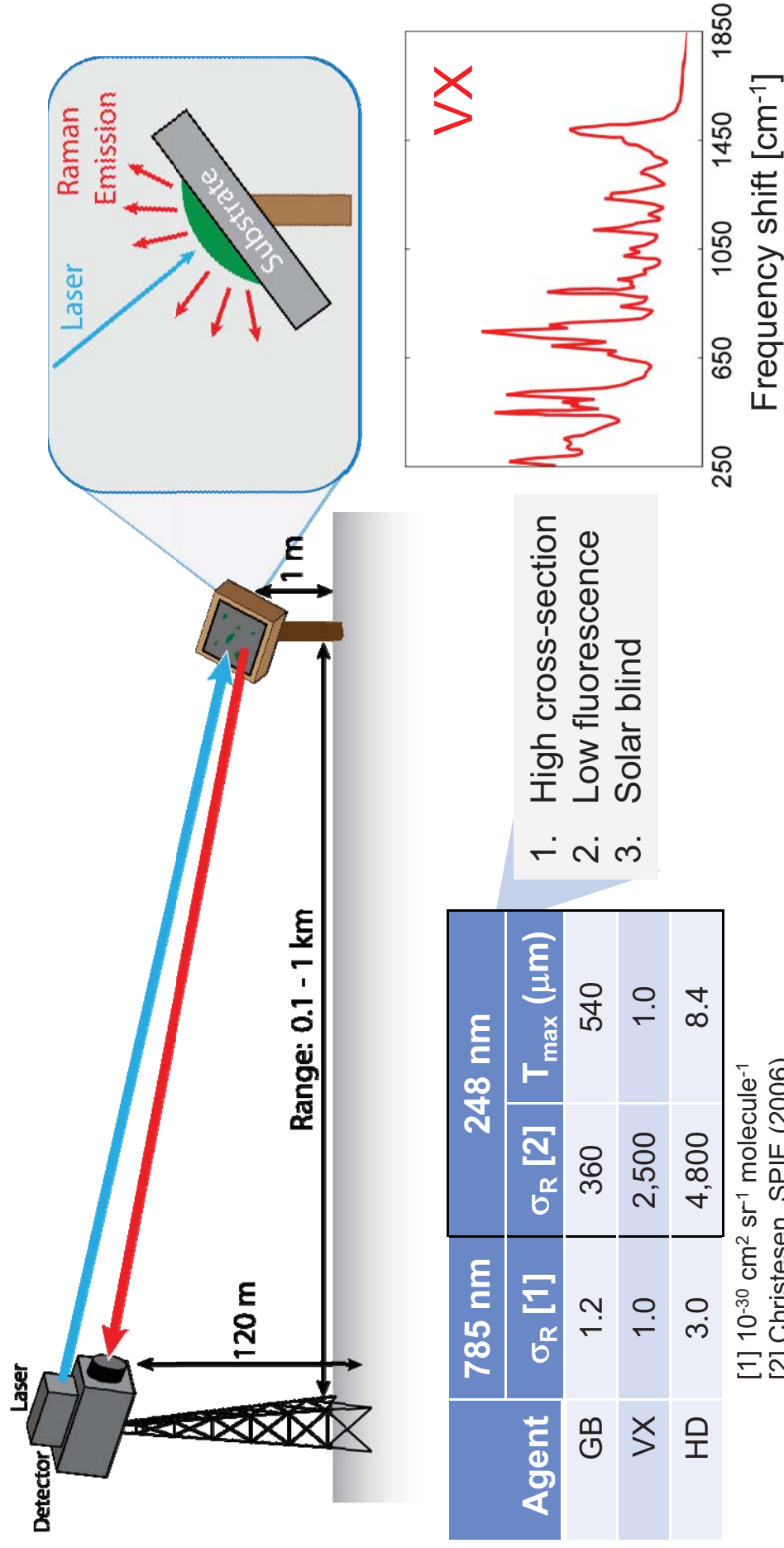
- Fixed site scenario allows unique opportunities for “remote” detection of contaminants
- Designing substrates for pre-placement around Fixed Site could enhance detection:
  - Known background to simplify analysis
  - Coatings engineered to optimize wetting
  - SERS substrates for Standoff Raman
  - Retroreflectors for Active LWIR detection
- Known, pre-interrogated substrates minimize effects of clutter





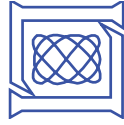


# Raman Setup



Analysis will focus on Raman excitation in UV region ( $\lambda = 248\text{nm}$ )





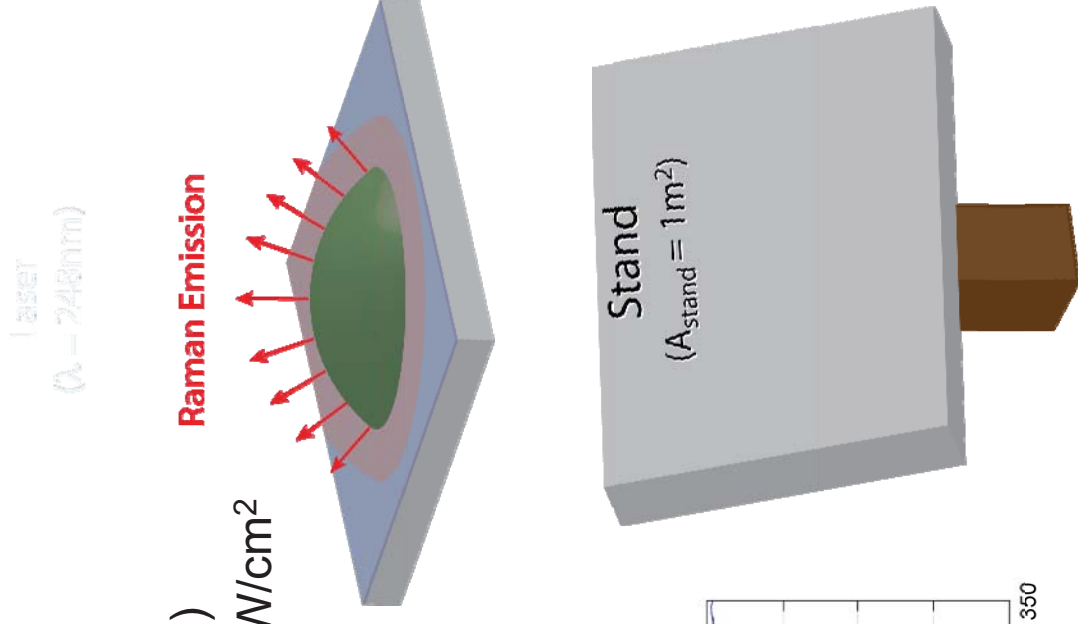
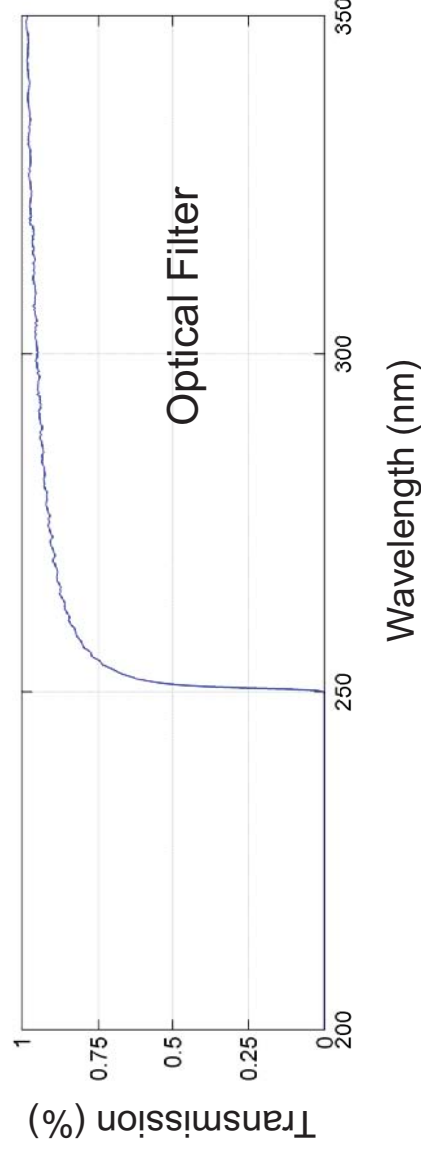
# UV Raman Analysis

## Transmit:

- Illuminate entire stand w/ laser ( $\lambda = 248\text{nm}$ )
- 437 stands interrogated in 25 minutes ( $\tau = 3.5\text{s}$ )
- Eye Safe Power ( $\lambda = 248\text{nm}$ ,  $\tau = 3.5\text{s}$ ):  $0.86 \text{ mW}/\text{cm}^2$

## Receive:

- Aperture size:  $D = 0.203\text{m}$  (8")
- Assume entire stand is one pixel
- Majority of returning photons are at  $248\text{nm}$
- Filtering used to keep only shifted photons





# UV Raman Analysis

## Signal Model:

$$e_{255}^- = QE \cdot \Omega \cdot \tau \cdot P_{\text{laser}} \cdot \sigma_R \cdot \frac{\text{Molecules}}{A_{\text{stand}}}$$

Where:

QE = Detector Quantum Efficiency

$\Omega$  = Solid angle (sr)

$\tau$  = integration time (seconds)

$P_{\text{laser}}$  = Laser power in photons per second

$\sigma_R$  = VX Raman cross-section =  $2.5 \times 10^{-27}$  cm<sup>2</sup>/molecule

$A_{\text{stand}} = 1 \text{ m}^2$

$$\text{Molecules} = N_{\text{drop}} \cdot SA_{\text{drop}} \cdot t_p$$

Where:

$N_{\text{drop}}$  = Number of drops on stand

$SA_{\text{drop}}$  = Surface Area of individual drop

$t_p$  = penetration depth at 248nm in VX =  $1 \mu\text{m}$

## Signal + Noise Model:

### Noise Sources:

- Shot Noise
- Detector Dark Noise
- Readout Noise

$$\mu_{\text{signal}} = e_{255}^- + e_{\text{Dark Noise}}^- + e_{\text{Read Noise}}^-$$
$$\sigma_{\text{signal}} = \sqrt{e_{255}^- + e_{\text{Dark Noise}}^- + (e_{\text{Read Noise}}^-)^2}$$

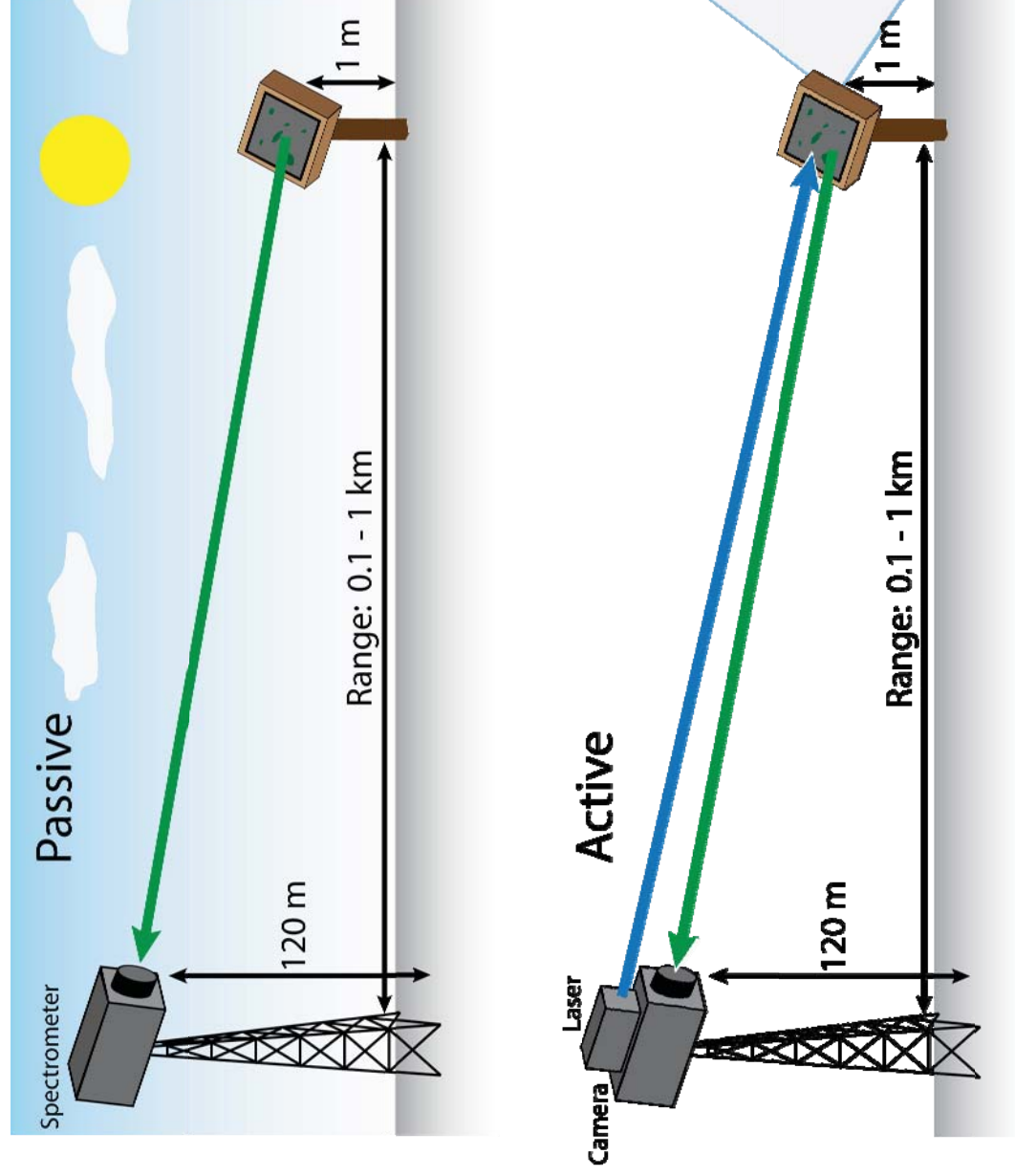
**Simple detection algorithm:**

If  $\mu_{\text{signal}} \geq \text{threshold}$

**ALARM**



# Active and Passive LWIR Setup





# Active LWIR Analysis

## Transmit:

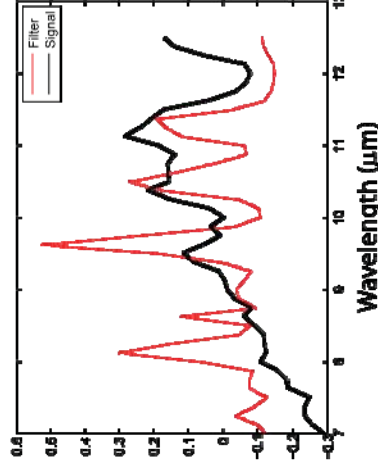
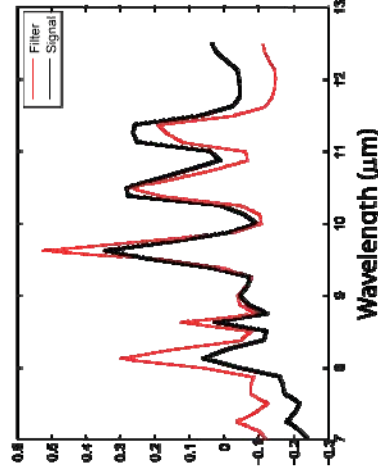
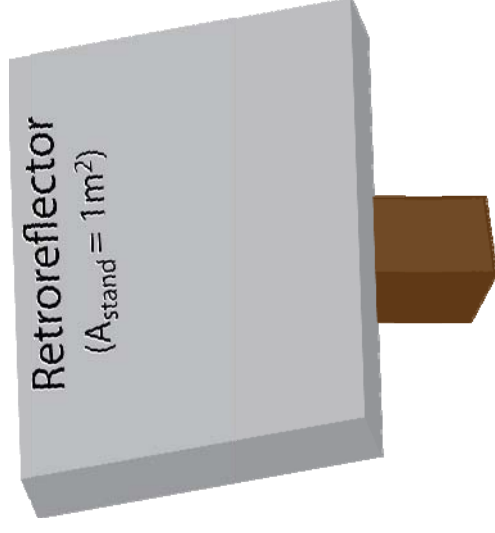
- Illuminate retroreflector w/ tunable laser
- 437 stands interrogated in 25 minutes ( $\tau = 3.5\text{s}$ )
- Signal-average 50 times during  $\tau$
- Eye Safe Power ( $\lambda$  in LWIR,  $\tau = 3.5\text{s}$ ):  $219\text{ mW/cm}^2$

$\lambda$ -tunable laser



## Receive:

- Aperture size:  $D = 0.203\text{m}$  (8")
- Assume entire stand is one pixel
- Clean signal subtracted from contaminated
- Spectral signature compared to matched filter





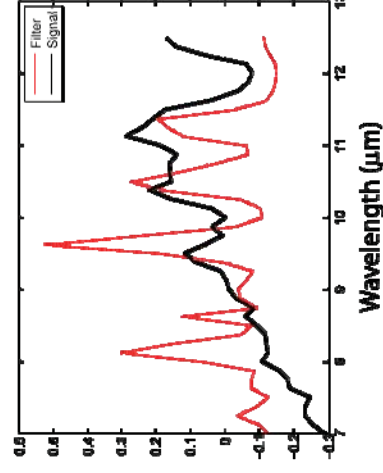
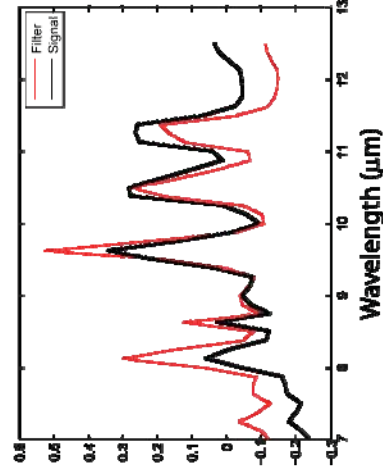
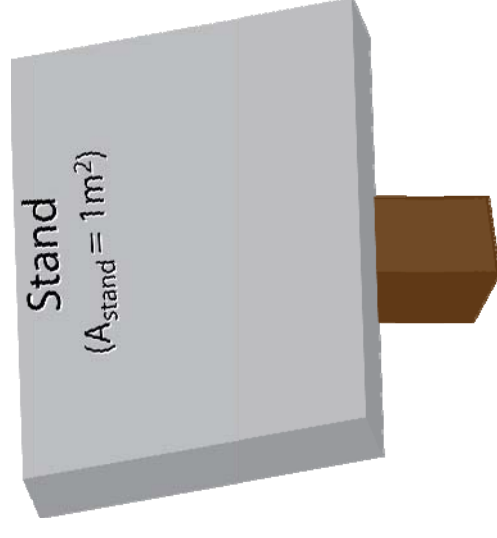
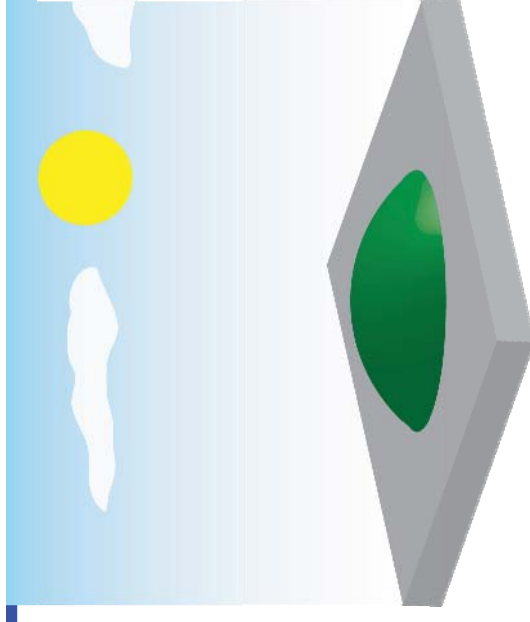
# Passive LWIR Analysis

## Transmit:

- 437 stands interrogated in 25 minutes ( $\tau = 3.5s$ )
- Assume  $50^\circ$   $\Delta T$  between substrate and sky
- Treat substrate and sky as black bodies

## Receive:

- Assume entire stand is one pixel
- Clean signal subtracted from contaminated
- Spectral signature compared to matched filter





# LWIR Analysis

## Signal Model:

Active:  $e^- = QE \cdot \Omega \cdot \tau \cdot f_{BRDF} \cdot (P_{laser} \cdot R + L)$

Passive:  $e^- = QE \cdot \Omega \cdot \tau \cdot f_{BRDF} \cdot L$

Where:

QE = Detector Quantum Efficiency

$\Omega$  = Solid angle (sr)

$P_{laser}$  = Laser power in photons per second

$R$  = Reflectivity

$f_{BRDF}$  = Bi-directional Reflectance Distribution Function ( $sr^{-1}$ )

$L$  = Radiance in photons per second

## Signal + Noise Model:

$$\mu_{signal} = e_{255}^- + e_{dark}^-$$

$$\sigma_{signal} = \sqrt{\mu_{signal}}$$

### Noise Sources:

- Shot Noise
- Detector Noise

$\alpha_{filter} = VX$  absorption matched filter

$$d\mu = \mu_{signal} - \text{mean}(\mu_{signal})$$

$$mf_{signal} = \frac{\mu_{signal} \cdot \alpha_{filter}}{\sqrt{(\mu_{signal} \cdot \mu_{signal})(\alpha_{filter} \cdot \alpha_{filter})}}$$

**Matched filter algorithm:**

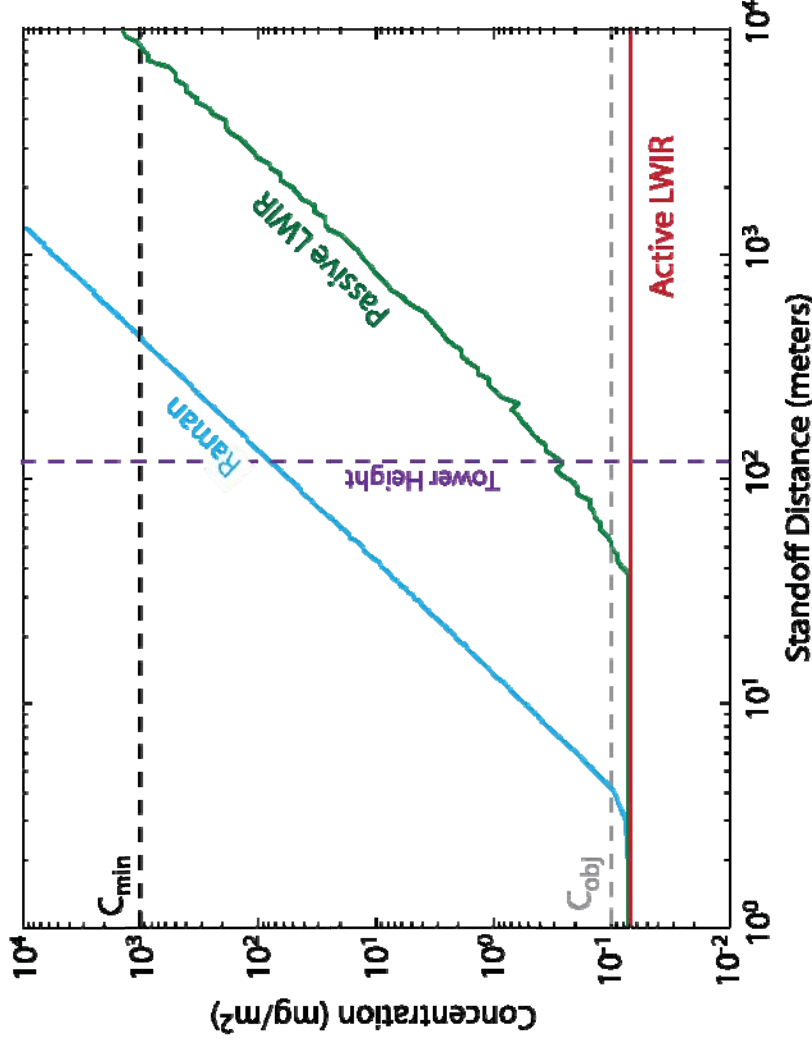
If  $mf_{signal} \geq \text{threshold}$

**ALARM**



# Fixed Site: Performance Curves

Detectable Concentration vs. Standoff Distance



- **Raman** is signal-limited and shows limited potential for detection at long range.
- **Passive LWIR** is also signal-limited at distances more than ~30 meters.
- Active LWIR on pre-placed retroreflective substrates shows strong potential for detection at long range

**Raman** is limited by physics, while

**Active LWIR** shows strong potential when clutter can be minimized





# Fixed Site: Potential Tiered Sensing Solutions



- Wide Area Coverage Detection  
(e.g. Central Tower or UAV)

- Detect and *potentially* ID contaminant from height of 100+ meters
- Map area of suspected contamination



- Standoff Spot Detection  
(e.g. UV Raman on Ground Vehicle)

- ID with high specificity from 10s of meters in area indicated by wide area sensor



- Short-Range Spot Detection  
(e.g. Raman and/or LIBS on UGV)

- Detect and ID lower levels of contamination with high sensitivity



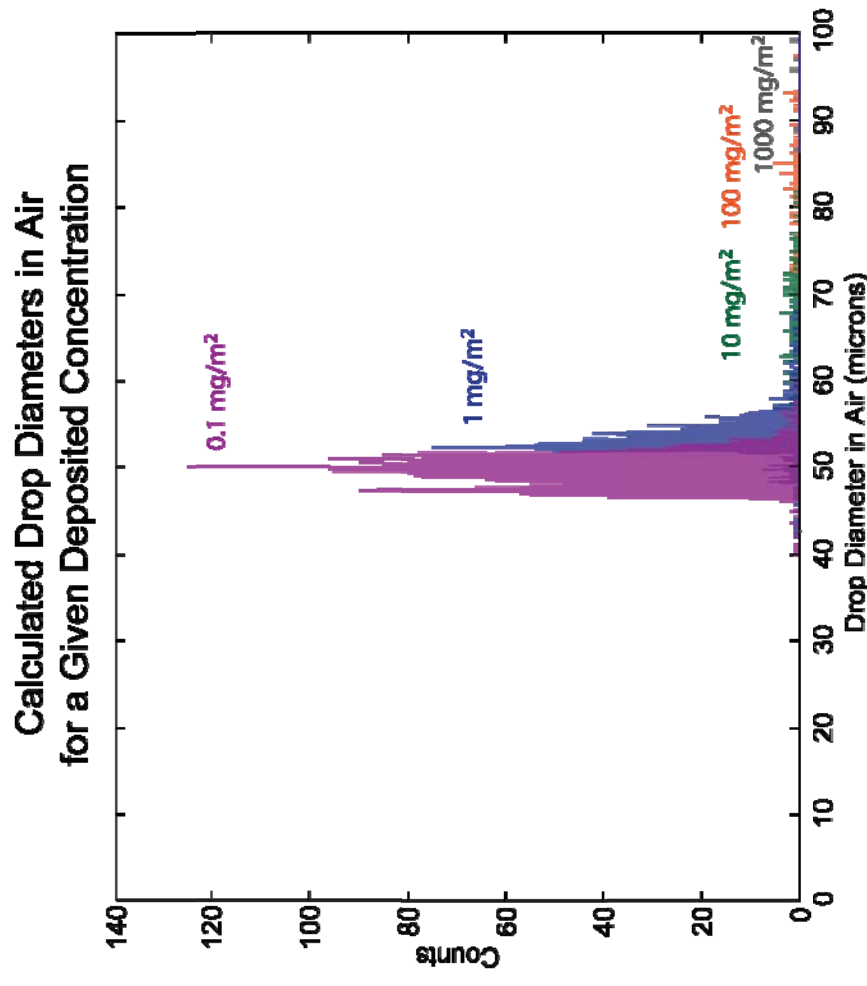
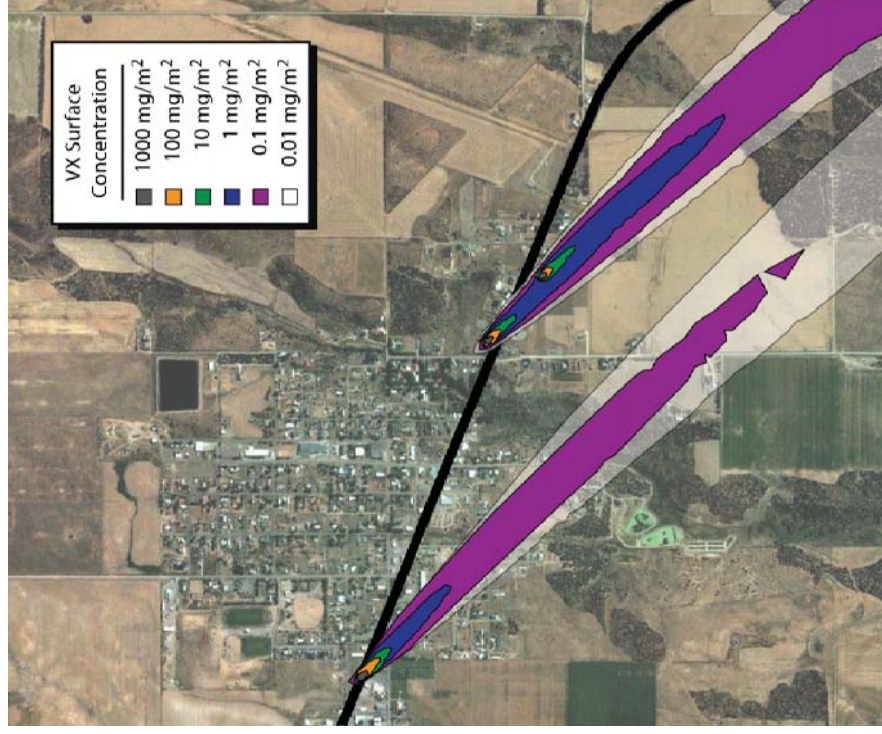
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- **Application to Scenarios: Maneuver**
  - Active and Passive LWIR Spectroscopy
- **Conclusions**



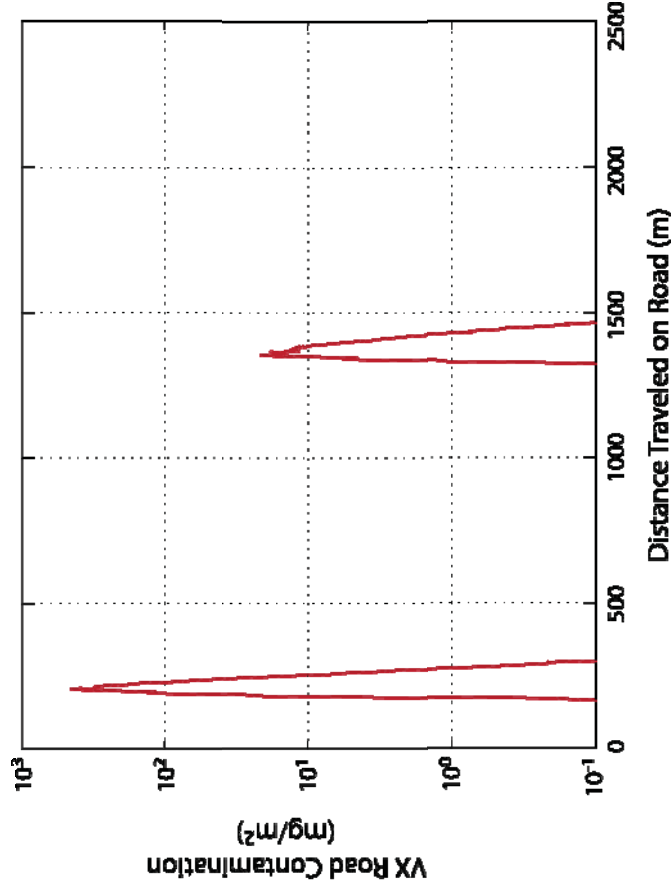
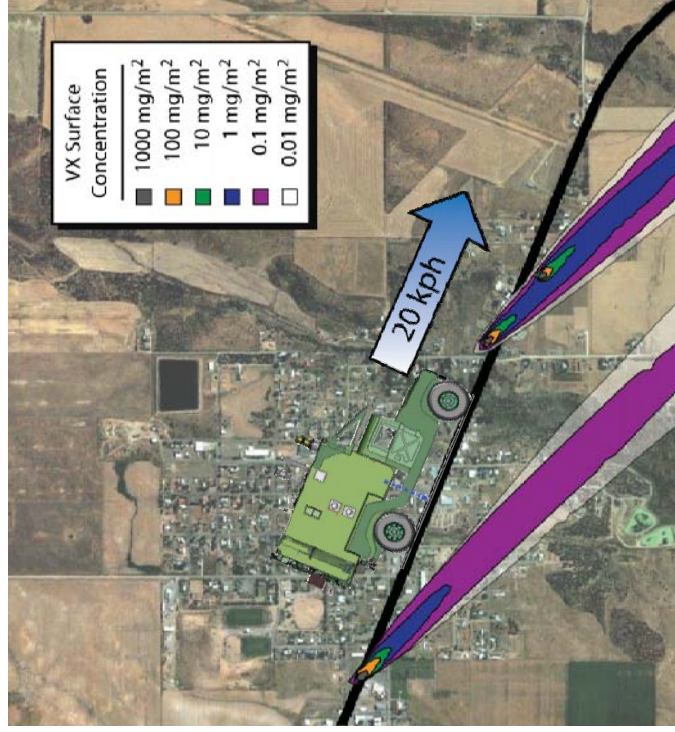
# Maneuver



- Baseline Technology: JCS
- Will attempt larger interrogation area, standoff detection



# Concentration Encountered



Assumes JCSD  $p_{\text{sensor}} = 1$

- Unlikely for drops < 100  $\mu\text{m}$  (even w/ wetting)
- However, shouldn't matter unless  $p_{\text{sensor}} < 0.01$
- More JCSD performance data needed

$p_{\text{drop}}$	VX Sprayer	1 JCSD	3 JCSD
Maneuver droplet sizes		100%	100%
Fixed site droplet sizes		52.4%	89.2%

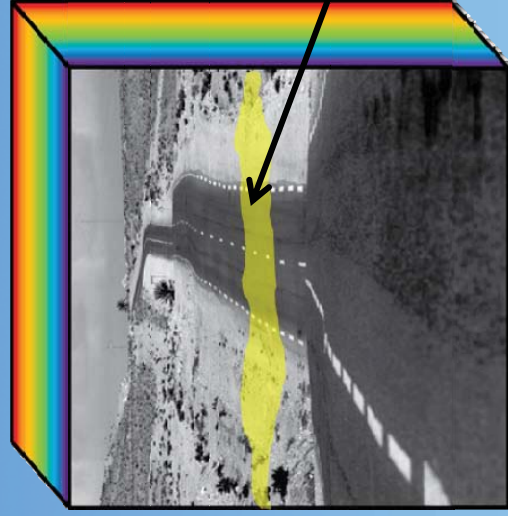
JCSD (as modeled) provides adequate warning for maneuver main force, however all scout vehicles expected to become contaminated





# Maneuver: Active and Passive LWIR

## Multispectral Image Cube

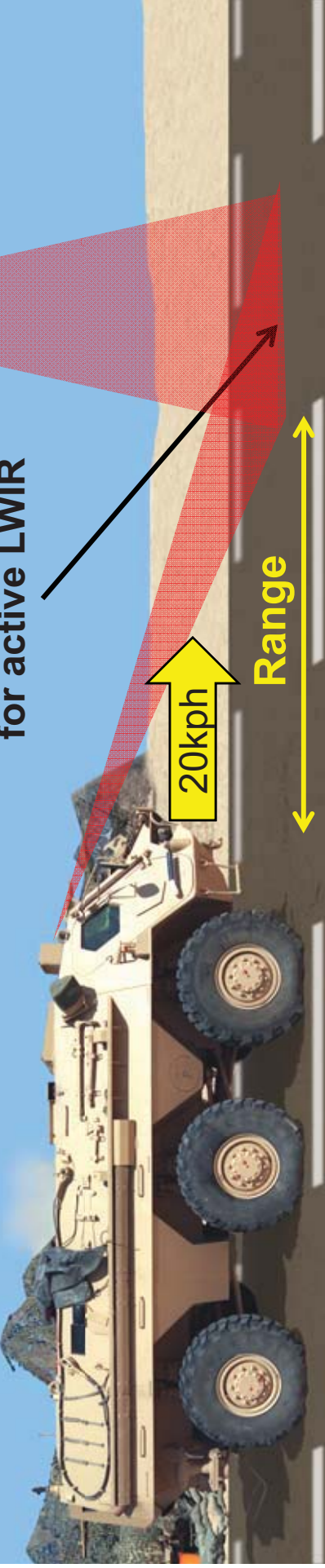


Detected agent

## Air Platform



## Ground Platform



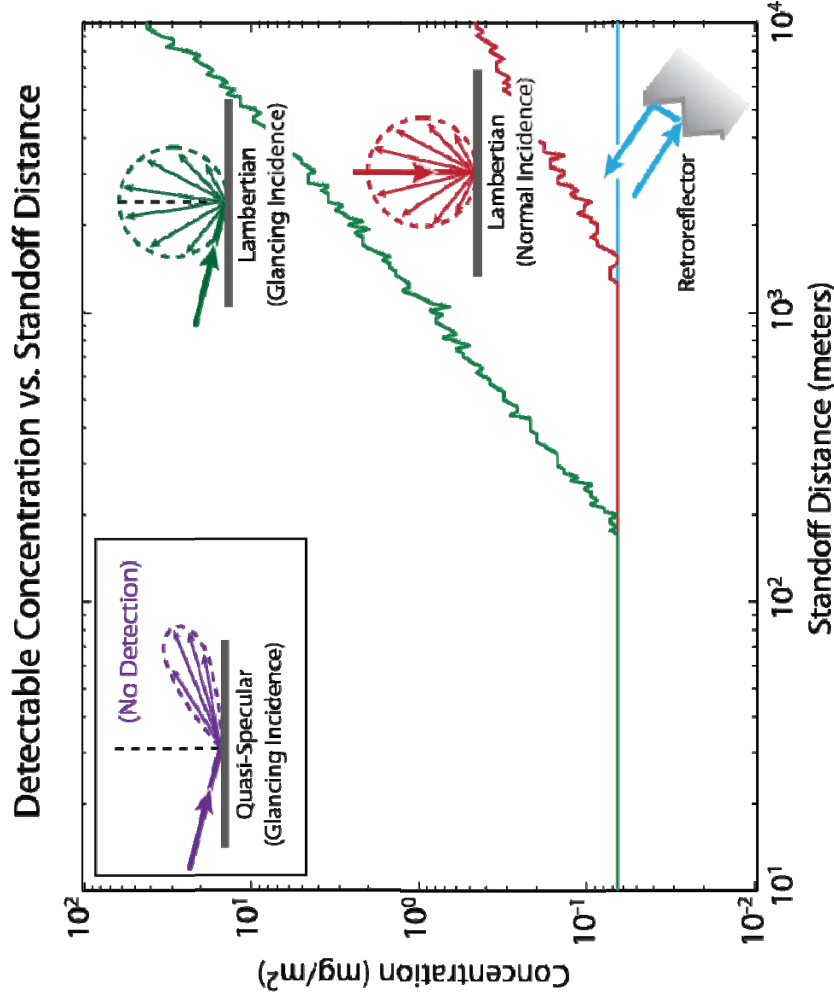
Illuminate scene  
for active LWIR

20kph

Range



# Maneuver: Angular Dependence of Active LWIR

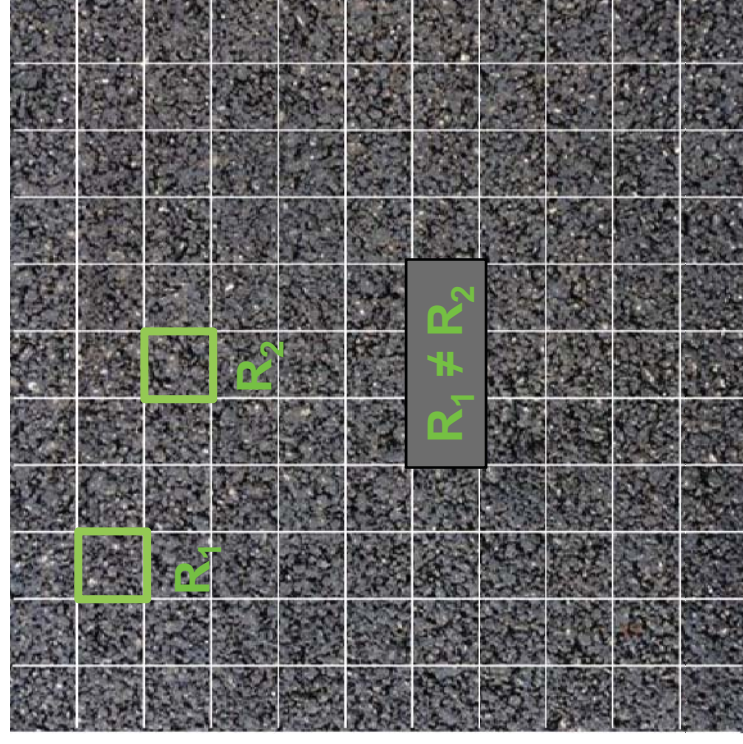
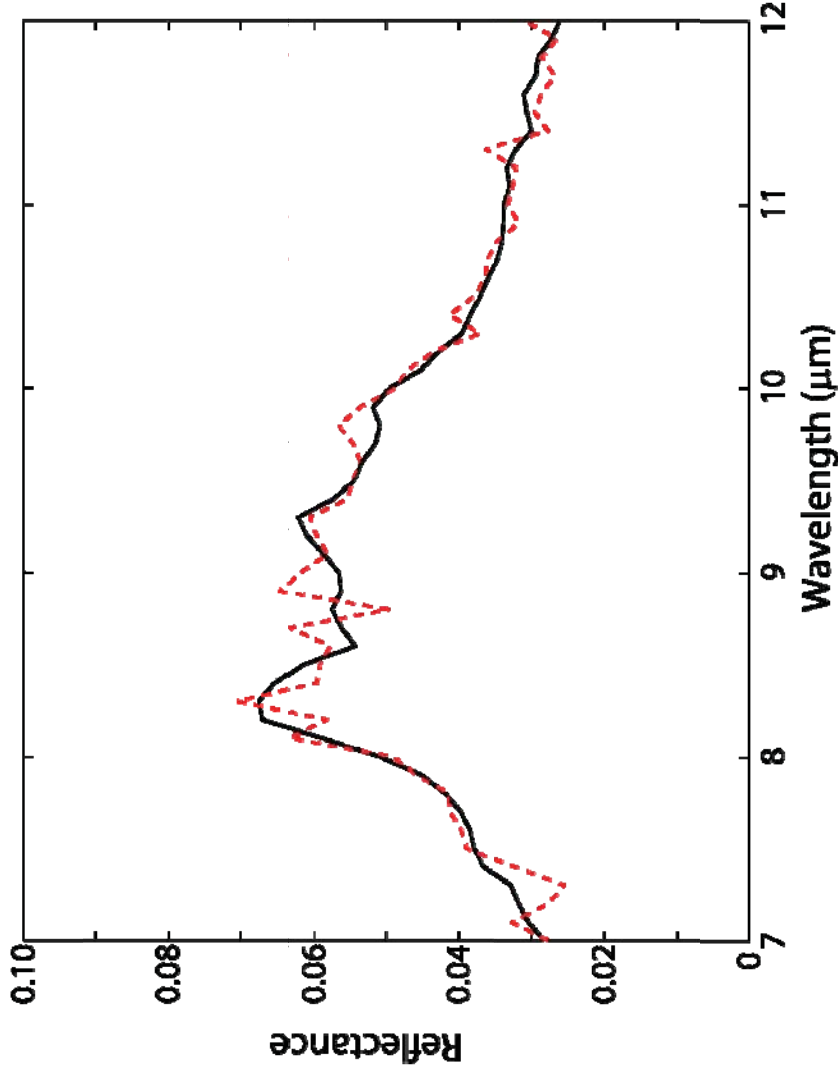


Signal returned from any given substrate will vary from large (e.g. a retroreflector) to nonexistent (e.g. quasi-specular substrate interrogated at a glancing angle)



# Maneuver: Reflectance and Clutter

Reflectance Profile - Weathered Asphalt



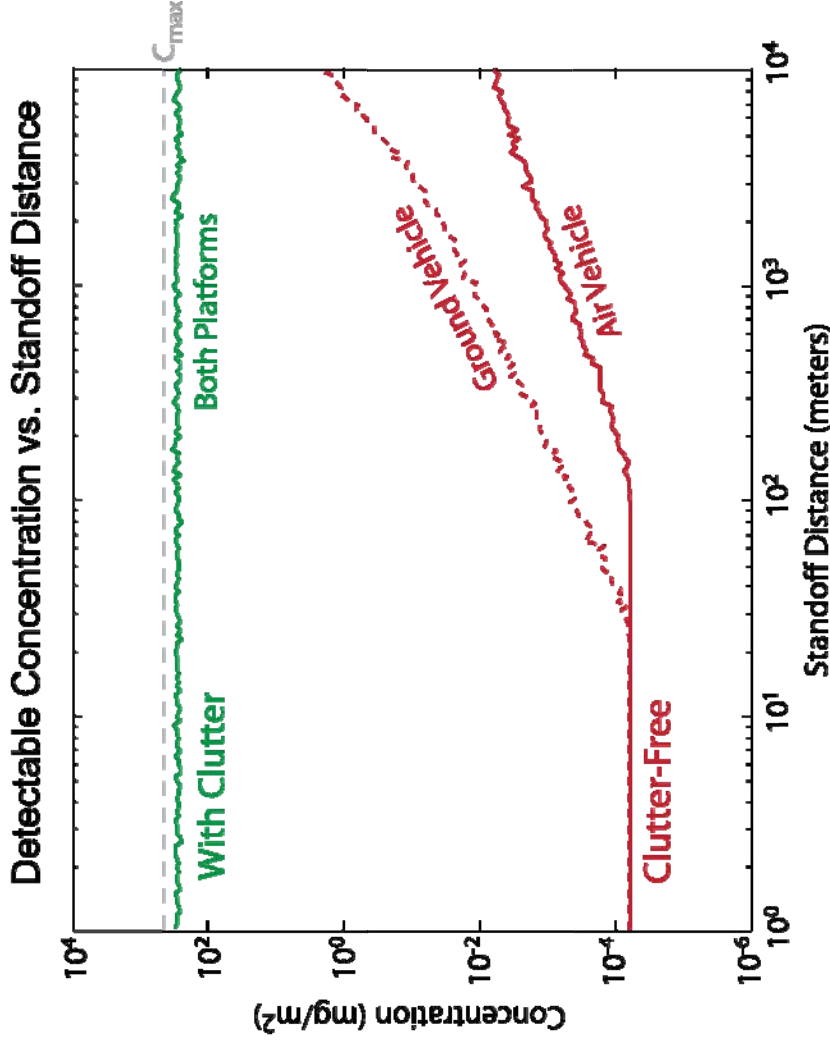
Substrate reflectivity will vary from pixel to pixel, introducing noise we refer to as “**clutter**” during background subtraction





# Maneuver: Active LWIR Performance

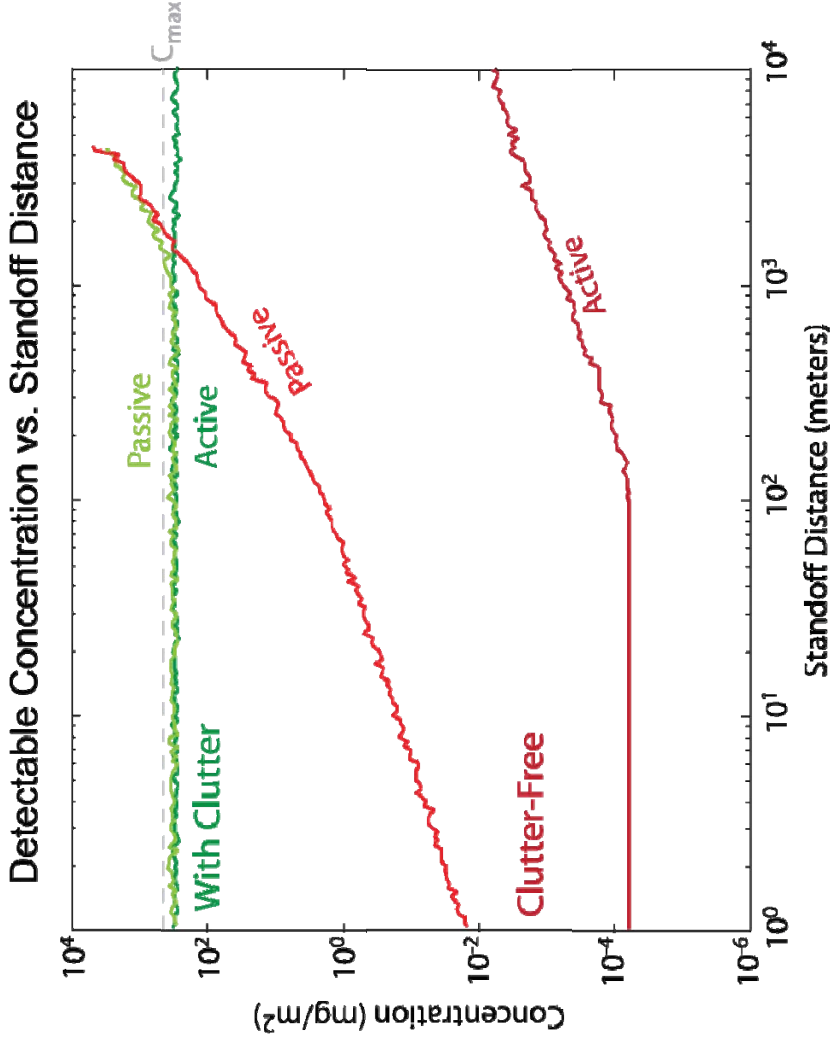
- In the absence of clutter, both platforms perform reasonably well
- With clutter, performance is clutter-limited and both platforms perform poorly
- Ability to detect only the highest concentration the vehicle is predicted to encounter, ground vehicle is likely to become contaminated



Air vehicle equipped with Active LWIR may have potential to detect areas of highest contamination



# Maneuver: Active and Passive LWIR Performance on an Air Vehicle



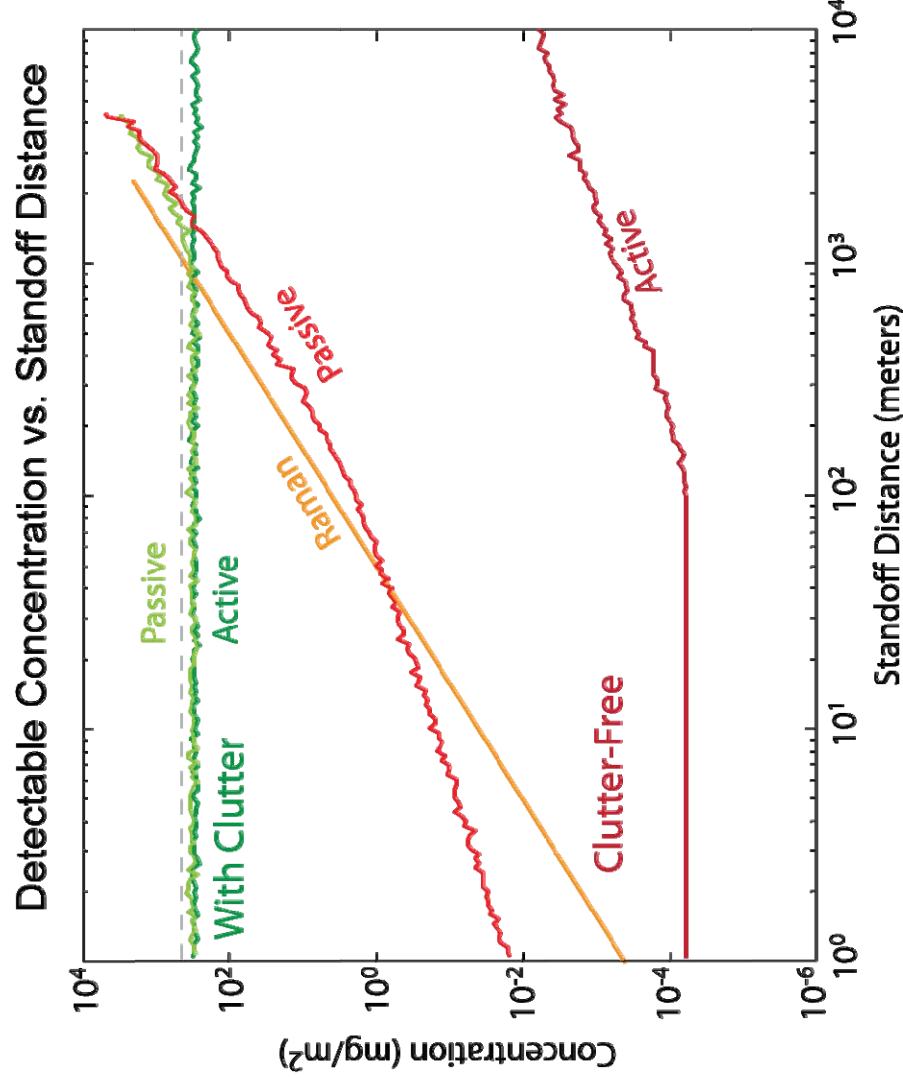
- In the absence of clutter, Active LWIR performs considerably better than Passive
- With clutter, both sensors are clutter-limited and both perform similarly
- Active (with large laser) not expected to offer any true advantage over Passive in the clutter-limited case

Air vehicle equipped with Active or Passive LWIR may have potential to detect areas of highest contamination



# Maneuver: A Word about Raman

- Raman was initially ruled out due to limited sensitivity at range (for eye-safe laser powers)
- Given the calculated performance of the LWIR techniques on the maneuver, Raman may be an equally viable candidate
- Will need to develop a more thorough Raman model to confirm utility in the presence of clutter





# Conclusions

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- Remote detection of chemical agents is challenging
  - Small drops on surfaces push sensors to very high spatial resolution
  - High spatial resolution impedes rapid, wide area coverage
  - Areal surface coverage can be low even at hazardous concentrations
- Fixed Site analysis shows potential for tiered sensing system
- “Remote” detection can be utilized on a Fixed Site to optimize detection capabilities in the fixed site scenario
- Standoff detection on the move is considerably more difficult
- Further analysis is required to assess all options



# Acknowledgements

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**Ben Ervin**  
**Michael Switkes (81)**  
**Anish Goyal (82)**  
**Amanda Schiff**  
**Steve Medaglia**  
**Dan Mooney (97)**  
**Ed Wack**